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ELECTRICAL RESISTANCE UNDER PRESSURE, INCLUD-ING CERTAIN LIQUID METALS.

By P. W. BRIDGMAN.

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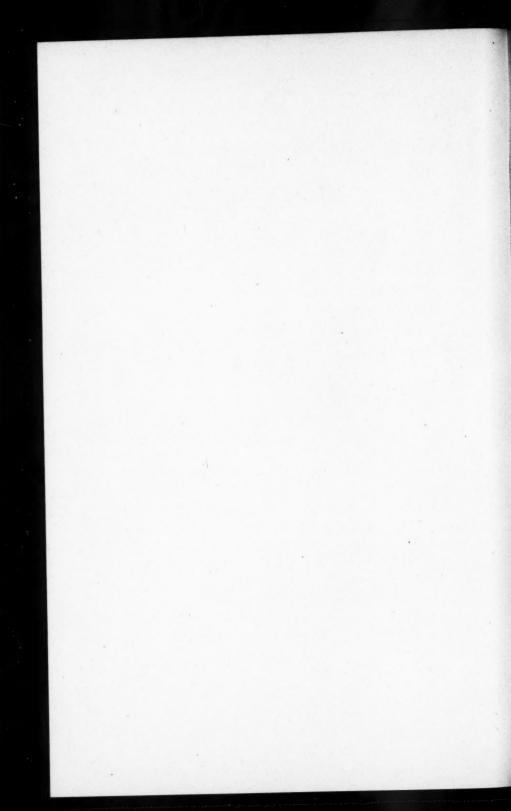
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Introduction.

In an earlier investigation ¹ I have determined the effect of pressure on the resistance of a number of the metallic elements, and have considered the significance of the results for theories of metallic con-

duction. The results then obtained suggested a number of important questions which could not then be answered because the data had not been determined. In particular, the effect of pressure on the resistance of only one liquid metal had been measured, mercury, and the comparative effect of pressure on the resistance of the same metal in the solid and the liquid state was not known for any substance. Furthermore, the effect of pressure on none of the alkali metals was known; it is just here that the largest effects would be expected and the most significant results for theory. The extension of the measurements to these substances demanded certain changes and improvements in the technique. I was soon able to make measurements on the alkali metals, and to my very great surprise found that the resistance of lithium increases under pressure, whereas that of the other alkali metals sodium and potassium decreases greatly. It was obvious that our pictures of the mechanism of conduction are not yet so perfect that we can reason by analogy even from one element to another closely related in the periodic table. The importance of making actual measurements on as many of the elements as possible, particularly the rarer ones, was obvious.

In the present work I have therefore attempted to extend the previous measurements to as many new elements as the new resources of my technique, and the availability of the elements themselves has made possible, with especial reference to the question of the resistance of the metals liquid within a moderate temperature range. Furthermore, a number of commercial alloys have been employed in other work, and rough measurements of the effect of pressure on the resistance of them have been necessary; it has been an easy matter to make the measurements precise enough to be included here. Of course the entire question of the effect of pressure on the resistance of the alloys is a most complicated one, and these isolated results cannot as yet have much significance.

The results given here are for eighteen new elements and six commercial alloys. In addition, better results than were possible in the previous work are here given for tungsten and magnesium. Better results on tungsten were possible because of the availability of purer material, and for magnesium the new technique makes possible the elimination of contact resistance, which introduced very large error in the previous work.

EXPERIMENTAL METHOD.

The metals measured in the previous investigation could all be made into wire of small diameter, and therefore high resistance, and nearly all of them could be soldered. The resistance was measured on a Carey Foster bridge. It was essential to accuracy that the resistance be so high and the contacts so good that the relative changes in contact resistance under pressure were negligible. Very few of the metals of this investigation satisfy this condition. For the measurement of the effect of pressure on the resistance of these, some sort of potentiometer method is indicated. The resistance of the contacts then is without effect, and relatively small changes on small resistances can be measured accurately.

The application of a potentiometer method demands four leads to the pressure chamber, two current leads, and two potential leads. Three of these leads must be insulated from the pressure chamber; the fourth may be grounded on the walls. An insulating plug carrying three leads was used in this work. It is an obvious modification of the single terminal plugs previously used. It may be mentioned that the modification of the design of the plug suggested on page 641 of the paper referred to, making possible the use of the ring packing, has been in use now for a number of years, and was used with the new three terminal plug. The chief difficulties encountered in the three terminal plug were the mechanical difficulties of securing the accuracy required in getting three terminals into a small space. The fine insulated stems were made of piano wire 0.032 inches in diameter, held into a head at the top by a special wedge grip. Each of these stems with its head was tested before assembling with a tension of 270 pounds, corresponding to a pressure of over 20,000 kg/cm². Without a preliminary test there is danger that the stem will pull out of the head under pressure. The mica washers used for insulation of the plug were punchings, made a tight fit for the hole, which was 0.209 inches diameter. They were forced into place in the plug, and drilled concentrically for the stem with suitable jigs after they were in final position. Later the mica washers have been replaced with pipe-stone washers with more satisfactory results. The chief difficulty encountered with this plug has been in using it near 100°. Here the rubber insulation gives out under the action of the petroleum ether with which pressure is transmitted, and the insulation has to be renewed much more frequently than with the larger plug.

The method of electrical measurement is a null substitution method. In series with the material under pressure is a second resistance, part of which consists of a slide wire. By means of a variable slider, it is possible to tap off a variable part of this second resistance. A throw-over switch enables either the potential terminals of the pressure coil or the variable part of the series resistance to be connected to the indicating galvanometer. This galvanometer is a Leeds and Northrup high sensitivity moving coil instrument. At the scale distance used its sensitiveness was 10^{-9} volts; its sensitiveness could be decreased with appropriate shunts.

The measurements are made by adjusting the various resistances so that there is no change of deflection on operating the throw-over switch. The resistance of the pressure coil may then be computed from the known values of the other resistances. In practise, sensitiveness and speed of operation are increased by throwing into the galvanometer circuit another e.m.f. approximately equal and opposite to the potential difference across the pressure coil, so that the actual deflection is approximately zero. This balancing e.m.f. should be variable over a wide range and should be fairly constant. To produce it, I used the apparatus previously used in measuring thermal e.m.f. under pressure, tapping across the former pressure terminals. The refinements of that apparatus were not necessary, but it was easier to use apparatus already at hand than to construct new. The apparatus by which the variable balancing e.m.f. was applied is indicated by VE in Figure 1.

The details of the connections are shown in Figure 1. When adjustments are made we know that the potential drop around R (the pressure coil, which is usually a small fraction of an ohm) is equal to that about R_3 plus r_1 . This latter drop of potential may be computed from the known values of R_1 , R_2 , R_3 , r_1 , and r_2 , and gives

$$R = \frac{R_1(R_3 + r_1)}{R_1 + R_2 + R_3 + r_1 + r_2}.$$

The resistance r_1 (and r_2 accordingly) is the only resistance varied during a pressure run; the other resistances R_1 , R_2 , and R_3 being appropriately chosen and then kept constant during each run. Since $r_1 + r_2 = r$ (a constant) we have, for any one run,

$$\Delta R = C \Delta r_1$$

or, putting $R=R_0+\Delta R$, and writing r_{10} for the initial value of r_1 corresponding to $R=R_0$

$$\frac{\Delta R}{R_0} = \frac{\Delta r_1}{R_3 + r_{10}} = \frac{\Delta l}{L_3 + l_0}$$

where L_3 is the length of the slide wire having the resistance R_3 , and l_0 and Δl are the actual readings of the slide wire. This arrangement therefore, gives immediately in terms of slide wire settings the proportional change of resistance under pressure. If R_3 is kept constant for the runs on the same metal at different temperatures, making the necessary adjustments in passing from one temperature to another by changing only R_1 and R_2 , the readings give directly a comparison of the pressure coefficients at different temperatures without demanding a knowledge of how the resistance itself varies with temperature. This was the procedure followed in this work; the pressure coefficients

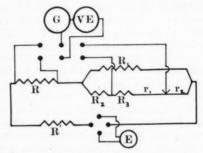


FIGURE 1. The electrical connections by which resistance is measured. The resistances are so adjusted that the potential drop across R is equal to that across $R_3 + r_1$.

are therefore independent of any error in the temperature coefficient of resistance at atmospheric pressure.

In actual construction, all parts practical were made of copper. The resistances R_1 and R_3 were fixed coils dipping in mercury cups in $\frac{3}{4}$ inch copper bars. The apparatus was so designed that all terminals were within a few inches of each other, in order to avoid thermal effects. The slide wire was of manganin. The slider was also of manganin, and was attached by soldering to a flexible many-stranded manganin wire making connection at the other end to a copper block surrounded by the bars containing the other terminals. By soldering the flexible manganin lead to the slider very close to the point of contact with the slide wire, thermal electromotive forces in this part of the circuit were very largely avoided.

The effect of parasitic electromotive forces in the circuit was eliminated by taking the mean of readings with direct and reversed potentiometer current. A reversing switch was supplied for this purpose, as also in the circuit of the balancing variable e.m.f. The only requirement in the potentiometer current is that it shall remain constant during the substitution of the pressure coil for the slider. The substitution was made rapidly by a double throw switch, so that an ordinary dry cell was entirely good enough as the source of the potentiometer current.

The function of the resistance R^1 (Figure 1) was merely to provide an additional adjustment by which the deflection of the galvanometer might be easily made null. An ordinary decade box was good enough

for this.

The usual procedure was as follows. A preliminary examination indicated the order of the pressure effect. R_3 was then so chosen that the motion of the slider would be of the order of 40 cm. for the entire pressure range, the total length of the slide wire being 60 cm. R_1 and R_2 were then so chosen, depending on the actual resistance of the pressure coil, that the galvanometer deflection was unaltered on substituting the pressure coil for the slide wire. The following coils for R_1 and R_3 usually gave sufficient range of choice; two 0.5 ohm coils, two 1's, and one each of 2, 3, 4, 10, 20, and 30 ohms. For R_2 a plug box from 0.1 to 1000 ohms was used. R^1 was then set at about 2000 ohms, or less if the parasitic e.m.f.'s, were troublesome, and the balancing e.m.f. adjusted to give no deflection. These adjustments were preliminary to the application of pressure. The adjustments after each change of pressure were, first, an adjustment of R^1 to give again approximately null deflection when the pressure coil is in circuit, second, setting of the slider to give no change in deflection on substitution, third, reversal of the potentiometer current and the balancing e.m.f. and resetting of the slider for no change of deflection, and fourth, change of the potentiometer current and the balancing e.m.f. back to their original directions and again setting the slider. By taking an odd number of readings the effect of any slow change of the parasitic e.m.f. due to dissipation of the heat of compression was eliminated. The potentiometer current was usually so chosen that the difference of slider setting for the two directions of the current occasioned by the parasitic e.m.f. was less than 1 cm.

The coils were all compared with standards and proper corrections applied. The slide wire was calibrated and corrections applied for lack of uniformity. In general, all the precautions of manipulation

and construction previously employed in measurements of resistance or thermal e.m.f. under pressure were observed here also.

The methods of computation were essentially the same as those which have been described in great detail in the previous paper. Any slight modifications were entirely obvious, and it is not necessary to describe them further.

A description in detail of the results obtained for the separate substances now follows.

DETAILED DATA FOR INDIVIDUAL SUBSTANCES.

LITHIUM. Two distinct series of measurements were made on this substance, at two different times. The first series was on the pressure coefficient of the solid, in the spring of 1919. It was found that the pressure coefficient is positive, and large. This result was so surprising in view of the high compressibility of the metal, and its close relation to sodium and potassium, both of which have a very high negative-coefficient, that a correlation of this positive coefficient with other properties of lithium was desirable. For instance, does lithium expand in freezing, like bismuth, and if so, is this connected in any way with the positive coefficient? But on looking up the data I could not find that the melting data for lithium had ever been determined. It was not even known whether lithium expands or contracts on melting. The second series of measurements, in the winter of 1919-20, was concerned with the effort to obtain some of the missing data. particular, it was desirable to find the volume relations on melting, and to find whether the pressure coefficient of the liquid is positive as well as that of the solid. I had already found that the positive coefficient of solid bismuth changes to negative on melting.

The first series of measurements, on the resistance of the solid, was made on lithium from Merck, prepared a number of years ago, but kept under oil in sealed glass since then. A chemical analysis by Mr. N. S. Drake showed 0.7% Al, and a trace of Fe. Sodium, if any, could not be determined because only one gram of the lithium was available for analysis. The method of preparation by electrolysis should not allow much impurity of sodium if ordinary care is exercised.

The lithium was extruded cold through a steel die into wire 0.030 inches in diameter, and wound bare onto a bone core. Connections were made at the ends with spring clips. So far as I am aware, no previous measurements have been made on the properties of bare

lithium wire, but because of danger of oxidation, the lithium has been usually enclosed in a glass envelope. Measurements in glass, such as that of temperature coefficient of resistance for example, are not entirely free from objection, because of the constraining action of the glass walls. The error introduced by effects of this sort is presumably not large, but it is nevertheless gratifying to be able to avoid it.

A somewhat special technique is necessary to handle the bare wire successfully. It must, of course, be protected at all times from direct contact with the air. This was accomplished at first by extruding it directly into melted white vaseline, and winding it directly from the pot of vaseline onto the bone core, which was mounted for slow rotation by hand. The wire, in passing from the pot of vaseline to the bone core, becomes covered with a capillary film of vaseline, which rapidly solidifies in the air, forming a perfectly protecting coating. Later, however, the vaseline was replaced with a mixture of "Nuiol," which is a carefully refined heavy hydrocarbon, prepared by the Standard Oil Co. and sold as a remedy for constipation, and refined paraffine, melted together in such proportions as to have about the consistency of vaseline. This mixture was suggested to me by Dr. Conant of the Chemistry Department. This change was made necessary by the chemical action of the vaseline. The vaseline of commerce is not a substance of standardized properties; the first can of vaseline which I tried was without appreciable chemical action, but the second was unpleasantly corrosive in its action. The mixture of Nujol and paraffine was much more satisfactory, the lithium remaining bright for days.

The liquid transmitting pressure must also be chosen with care in order to avoid chemical action. At first I used commercial kerosene which had been standing in contact with sodium for several weeks. This was not satisfactory, however, the kerosene gradually turning yellow at room temperature in contact with the sodium, and at higher temperatures the reaction is much accelerated. The transmitting medium finally used was a mixture of Nujol and "petroleum ether" in different proportions, depending on the temperature of the work. At 0° nearly pure petroleum ether must be used in order to avoid freezing under pressure. Another source of chemical action, besides the transmitting medium, is the bone core on which the wire is wound. It is necessary to drive the water as completely as possible out of the core by prolonged heating to 130° or so, but under these conditions the bone becomes very brittle and must be handled with extreme care. Even after every precaution had been taken, some chemical action still

remained. The action tends to cease at the higher pressures. Error from chemical action was eliminated as far as possible by taking the means of readings with increasing and decreasing pressure, and at the higher temperatures by never releasing the pressure to atmospheric, but obtaining the zero reading from an extrapolation of the readings at higher pressures, where the chemical action is slower. The technique in handling sodium was the same as that used for lithium. It is a curious fact that although the chemical action of the mixture of Nujol and paraffine at atmospheric pressure is considerably less on the lithium than on the sodium, at higher pressures the reduction of the action is considerably greater in the case of sodium, so that the zero shift after a run at higher pressures and temperatures was greater in the case of lithium than sodium.

Runs were made on the effect of pressure on the resistance of the bare wire at 0°, 25°, 50° (partial run), 75°, and 96°. The difference between readings with increasing and decreasing pressure decreased uniformly from zero to the maximum pressure, instead of being almost entirely confined to the zero reading, as was the case with sodium. The zero shifts were 7% of the total effect at 0°, 5.5% at 25°, 7.8% at 75° and 18% at 96°. The run at 50° was not completed because of accident. In spite of the large zero shifts, the mean of the readings with increasing and decreasing pressure ran smoothly, and should be only little affected by the chemical action.

The temperature coefficient of resistance at atmospheric pressure was obtained from a coil of bare wire similar to that of the pressure measurements. In order to avoid as much as possible the effect of chemical action, four thermostats were kept running simultaneously at 0°, 25°, 50°, and 75°. The coil was immersed in a well of Nujol which had previously come to the temperature of the bath. After a reading at one temperature the coil was transferred in a few seconds to the bath at the next temperature, and readings made after a fixed constant interval. Seventeen minutes proved to be sufficient for acquiring complete thermal equilibrium. Readings were made successively from 0° to the maximum and back to 0° again. The mean of the ascending and descending readings should be free from error from chemical action. The zero shift after the run was 2.8% of the total effect, against 5.4% for sodium. The average coefficient between 0° and 100° was 0.00458. Bernini² found for lithium in glass the mean value 0.00457 between 0° and 177.8°. He found the relation between temperature and resistance to be linear. I found the resistance to increase more rapidly at the higher temperatures;

this would mean an average coefficient between 0° and 177.8° even larger than 0.00458.

The independent pressure runs at different temperatures did not fit as smoothly together as they frequently do, but the pressure effect varied irregularly from one temperature to another. Within the limits of error a dependence of pressure coefficient on temperature could not be established, and in the finally smoothed results the pressure coefficient is assumed independent of temperature. This demanded a maximum readjustment of the observed readings of 2.0% at 75°.

TABLE I.
RESISTANCE OF LITHIUM.

Pressure			Resistance		
kg/cm ²	00	25°	50°	75° .	100°
0	1.0000	1.1044	1.2122	1.3280	1.4580
1000	1.0069	1.1120	1.2206	1.3372	1.4681
2000	1.0140	1.1199	1.2292	1.3466	1.4784
3000	1.0212	1.1278	1.2379	1.3561	1.4889
4000	1.0285	1.1359	1.2468	1.3655	1.4996
5000	1.0360	1.1442	1.2558	1.3758	1.5105
6000	1.0436	1.1525	1.2651	1.3859	1.5216
7000	1.0514	1.1612	1.2745	1.3963	1.5329
8000	1.0594	1.1700	1.2842	1 4069	1.5446
9000	1.0675	1.1789	1.2940	1.4177	1.5564
10000	1.0757	1.1880	1.3039	1.4285	1.5683
11000	1.0841	1.1973	1.3142	1.4397	1.5806
12000	1.0927	1.2068	1.3246	1.4513	1.5932

Average coefficient 0 to 12000 kg, + 0.0 $_{5}772$. This coefficient is independent of temperature.

The values of the resistance of the solid at 25° intervals of temperature and 1000 kg. intervals of pressure are shown in Table I. The pressure coefficient is seen to be positive, as already noted. Furthermore, the pressure coefficients, both instantaneous and absolute, increase with increasing pressure. This we would not expect, but it seems to be the normal type of behavior for substances with positive coefficient.

The second series of measurements was made with another sample of lithium, much larger in amount, which I obtained through the kindness of Dr. A. W. Hull of the Research Laboratory of the General Electric Co. The purity was not known. It was prepared by electrolysis of the fused chloride with graphite electrodes; the chloride was pure, so that any impurities were introduced in the electrolysis. There were inclusions in it of some slag-like substance which had to be cut out as well as possible. This specimen was used for a determination of the melting curve. The method was that of the discontinuity of volume, which I have previously used in determining melting or transition curves, and has been fully described elsewhere. The volume of the specimen was about 5 c.c. It was placed in an iron container, and pressure transmitted to it with Nujol. It was evidently somewhat impure, for the corners of the melting curve were

TABLE II.

MELTING CURVE OF LITHIUM.

Pressure kg/cm ²	Temperature
0	178.4°
1000	182.1
2000	185.5
3000	188.8
4000	191.8
5000	194.6
6000	197.1
7000	199.4
8000	201.6

considerably rounded, melting being detectible at least 1000 kg. before the end of melting. This corresponds to a spreading of melting at constant pressure over a temperature range of 3.5°. What the depression of the freezing point is at the conclusion of melting, that is, how much the observed curve should be raised in order to correct for the impurity, it is not possible to state from the data. Points on the freezing curve were obtained at three temperatures. A curve was drawn through these points and the data from the smooth curve are given in Table II. The curve and the observed points are also shown in Figure 2. The points lie on the curve as drawn, but it is seen that there may be some uncertainty about the extrapolation to atmospheric pressure. The value of the melting temperature at atmospheric

pressure given in the Table was extrapolated from the three observed points on the assumption that $\frac{d^2\tau}{dv^2}$ is constant.

The most important result of these melting observations is that the melting curve is normal, pressure and temperature rising together. This means that the solid contracts on freezing, as is normal. The positive pressure coefficient of resistance of the solid therefore need not be due to the peculiar mechanism that it is in the case of bismuth.

The changes of volume on melting are very small, and because of the rounding of the corners, very hard to determine accurately. The error was too great to establish any regular variation of the change along the melting curve. The best mean value for the fractional increase of volume on melting is 0.006.

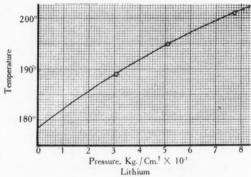


FIGURE 2. The melting curve of lithium.

The effect of pressure on the resistance of the liquid was measured on the same sample as that of the melting curve, the sample from Merck having been used up by the chemical analysis. Considerable difficulty was met in devising a suitable method. It is well known that melted lithium attacks glass, and this I verified by my own experience. Previous experimenters have been able to measure the resistance of the liquid in a glass capillary by protecting the interior surface of the capillary with a film of oil. This introduced error because of the space occupied by the film of oil, and is not adapted to use under pressure, the oil film being penetrated after a few compressions. The method finally adopted was to surround the lithium with

a capillary of an alloy of high specific resistance, which is not attacked by the lithium. For this purpose I used the allow known under the trade name of " #193 Alloy," manufactured by the Driver Harris Co. The specific resistance is about 50 times that of copper. I succeeded in drawing this into a fine capillary 0.045 inches outside diameter, and 0.032 inside diameter. An attempt to treat Nichrome similarly did not meet with such ready success, it being much harder to draw. The capillary was plugged at one end with a pin of iron, and at the other end an iron cup was silver soldered, no silver solder coming in contact with the lithium. Four copper leads were soldered to the outside of the capillary, two at each end, for use as current and potential leads, and the resistance was measured in the regular way by the potentiometer method. The capillary was filled by melting the lithium into it in vacuum. The resistance of the capillary was from five to ten times the resistance of the lithium which filled it, varying with the pressure and temperature. Preliminary measurements were made on the resistance of the capillary when empty, and on its temperature and pressure coefficients. These values for the capillary are given for themselves under the heading \$193 Alloy. The temperature and pressure coefficients are both small compared with those of lithium.

The capillary and the lithium inside it constitute two resistances in parallel. The various resistances are connected by the relation

$$\frac{1}{R_0} = \frac{1}{R_c} + \frac{1}{R_L}$$

where R_L is the resistance of the lithium filling the capillary, R_c is the resistance of the capillary alone, and R_0 is the observed resistance of the capillary and lithium in parallel. By differentiating this expression with respect to the pressure we obtain

$$\frac{1}{R_L}\frac{dR_L}{dp} = \frac{R_L}{R_0} \left(\frac{1}{R_0}\frac{dR_0}{dp}\right) - \frac{R_L}{R_c} \left(\frac{1}{R_c}\frac{dR_c}{dp}\right).$$

From the pressure coefficient as observed, and the pressure coefficient of the capillary separately determined, it is therefore possible to obtain the pressure coefficient of the lithium alone which fills the capillary. The term involving the pressure coefficient of the capillary is seen to be small, so that this coefficient need not be known with great accuracy, and the ratio of the resistance of the lithium to the observed resistance may be found with any accuracy desired, so that

the results should not have appreciably any larger error than the observed resistances themselves.

It is obvious that the temperature coefficient of resistance may be

found in a way precisely similar to the pressure coefficient.

Readings were made on the resistance of the liquid as a function of pressure at 202.5° and 237.4°. The pressure range of the lower temperature run was 8000 kg., since the melting curve restricts the domain of existence of the liquid, but at the higher temperature the pressure range was the entire 12000 kg. In order to avoid chemical action as far as possible, pressure was not released entirely to zero, but the minimum was about 1000 kg., and the results were extrapolated to zero. Measurements were also made on the solid at 171.6° to 8000 kg. (pressure was not raised higher for fear of distorting the capillary), and on the resistance of the solid as a function of temperature at atmospheric pressure down to 0°.

The most important result is that the pressure coefficient of the liquid is positive like that of the solid, reversing the behavior of bismuth. At the two temperatures the relation between pressure and resistance was linear within the limits of error of the measurements. At the lower temperature the maximum departure of any observed point from a straight line was 2% of the total effect, and at the higher temperature it was 1.3%. The coefficient is +0.05927, independent of temperature to the last figure. The coefficient of the liquid is seen to be slightly larger than that of the solid. The correction for the capillary brought the observed value from 0.05700 to 0.05927.

The temperature coefficient of the liquid, corrected for the capillary, was such as to give between 202° and 237° an increase of 0.00145 of the resistance at 202° for every degree rise of temperature. This is less than the reciprocal of the absolute temperature, giving, when multiplied by the absolute temperature, 0.689. The coefficient of the solid was found to be markedly higher than the reciprocal of the absolute temperature. This is again an example of the fact that the temperature coefficient of the liquid is in general less than that of the solid. Bernini ² found for the liquid between 180° and 200° a coefficient equal to 0.00077 of the resistance at 200°, considerably lower than the value above.

No correction has been applied to the above values for the compressibility or thermal expansion of the capillary, since these are not known. We have seen that the temperature correction is in general slight. If the compressibility of the alloy is the same as that of pure iron, which is a not unplausible assumption, the coefficient of the specific resistance will be about 2% less than the value above.

The pressure coefficient of the solid lithium was measured in the capillary at 171°. The most important result of this measurement was the verification of the positive coefficient. The numerical value of the coefficient cannot be accepted, however, because of the restraining effect of the capillary. A similar effect had already been met in the case of Gallium. The results for the resistance of the solid were very irregular, there being deviations of 10% from the mean curve. The value found for the coefficient was + 0.04159, nearly twice the value found at low temperatures for the bare wire. It is quite possible that part of this large difference is real, since we in general expect the coefficient to become larger at the higher temperatures. It was not possible to definitely state any variation of the coefficient within the range 0° to 100° for the bare wire, since chemical action cut down the accuracy of the measurements. It is also possible that some of the difference may be due to difference of the material, this latter specimen not being so pure. The pressure coefficient of the solid in the capillary was also measured at 94°, but the irregularities of the data were much greater than at 171°. One would expect the effect of constraint to become greater farther from the melting point. The best value of the coefficient at 94° was 25% higher than at 171°, but the accuracy was so low that it is not at all certain that there was any real difference.

The temperature coefficient of the solid in the capillary was also measured between 0° and 171°. Here again we should not expect the results to be very accurate because of the effects of constraint. The mean coefficient over this range was 0.0039. This is considerably less than for the unconstrained wire; part of the difference may be due to

greater impurity.

The change in the resistance on melting at atmospheric pressure could be computed from the measurements on solid and liquid separately. The specific resistance of the liquid is thus found to be 1.68 times that of the solid at the melting point at atmospheric pressure. The only other published value is by Bernini, who found 2.51. Bernini's value of the melting point was 177.84°, somewhat lower than the value given above, so that it is not probable that the difference is to be ascribed to greater purity of his sample. I also made an attempt to find the variation of the ratio of specific resistance of solid and liquid along the melting curve, but this cannot be very accurate, because of the constraining effect of the capillary. Using the value found for the pressure and temperature coefficients of the solid in the capillary, and assuming that the temperature coefficient is not affected by pressure (which has been proved to be true by direct measurement in most

cases), the resistance of the solid was extrapolated to the melting curve at 202.5° and 8430 kg., and at this point the ratio of resistance of liquid to solid found to be 1.49. The accuracy is not high, and probably the only conclusion justified is that the change of the ratio along the melting curve is not large.

Sodium. The material was from the same sample as that previously used in determinations of the change of melting point under pressure.4 No chemical analysis has been made, but the sharpness of the melting is evidence of the high purity. Two series of measurements of the resistance were made. The first, in the spring of 1919, was on the resistance of the solid below the melting point at atmospheric pressure. The second series, in the fall and winter of 1919-20, was on the resistance of both solid and liquid at temperatures above

For the measurements of the resistance of the solid below 97.6° the sodium was extruded into wire through a steel die, and the wire wound bare on a bone core. As in the case of Lithium, I am not aware that measurements have been made previously on the resistance of the bare wire, but the material has been enclosed in a glass envelope, The details of manipulation were essentially the same as for lithium, except that sodium is much softer, and consequently harder to handle. Two sizes of wire were used, at first 0.015 inches in diameter, and later 0.030. The larger size is considerably easier to handle, and the resistance is high enough to give the requisite accuracy. The initial resistance was of the order of 0.5 ohms for the small wire, and 0.2 ohms for the larger wire. Connections were made to the sodium wire with spring clips, as with lithium. The springs were helical springs of piano wire, 0.009 inches diameter, wound on a mandrel 0.06 inches diameter. The springs were pulled out so as to separate the spires, and the sodium wire dropped in between the spires. The wire was protected between the spires by wrapping round it a covering of gold or silver foil 0.001 or 0.002 inches thick; otherwise the soft wire is pinched off by the spring. Due to chemical action, the resistance at the spring contacts sometimes became so high as to make trouble. Contact could always be restored by passing through the contact a current from a small magneto.

Experiments were made on six different samples before a complete set of readings was obtained. Repetitions were necessary because of the effect of corrosion, and also because of accidents to the insulation of the three-terminal plug. In addition to complete runs at 0°, 25°, 50°, and 75°, one fragmentary run was made at 0°, and three at 50°.

These fragmentary runs have been given due weight in the final results.

No preliminary pressure seasoning of the wire was attempted. This is usually unnecessary for soft metals, and in this case was undesirable because of the effect of chemical action. The amount of chemical action may be estimated from the amount of the change of the zero after a run. At 0° the zero change was 5.6% of the total pressure effect; at 25° 8.1%; at 50° 1.9%, and at 75° at 1000 kg. 4.7%. The smaller effects at 50° and 75° are because the Nujol mixture was used at these temperatures to transmit pressure instead of kerosene. Since the readings with increasing and decreasing pressure were made at uniform time intervals, the mean zero should contain little error from corrosion. Aside from the zero displacements, the points at high pressures lay very regularly on smooth curves. At 0° the greatest departure of any point from a smooth curve was 1.6%; at 25° 1.3%, at 50° 0.8%, and at 75° 1.0%.

The final results were obtained by first smoothing independently the results at each temperature, and then smoothing the runs at each temperature so as to give smooth temperature differences. The maximum adjustment in this temperature smoothing was at 50° and 3000 kg., where an increase in the observed readings of 1.2% of the

total effect was necessary.

The temperature coefficient at atmospheric pressure was obtained from a coil of bare wire similar to that of the pressure measurements. The details of the measurements were exactly the same as for lithium. The two readings at 0° differed by 5.4% of the total temperature effect. The relation between temperature and resistance can be expressed by a second degree equation in the temperature. The results at even temperature intervals are included in Table III. The resistance of the solid at 100° (melting point 97.62°) may be extrapolated from readings between 0° and 75° and gives as the average temperature coefficient between 0° and 100° 0.005465. Northrup 5 gives for the temperature coefficient of sodium in glass the value 0.0053, obtained by a linear extrapolation of values between 20° and 93.5°. Bernini 6 gives for the same temperature range (0° to 100°) 0.00428. As already remarked, there seem to be no previous values on the unconstrained metal.

The measurements on the resistance in the domain of both liquid and solid above 97.6° were made with the sodium enclosed in a glass capillary. The details were exactly the same as for potassium. In point of time the measurements of potassium were made first, and the

TABLE III. RESISTANCE OF SODIUM.

1000 1.0000 1000 .9376 2000 .8830 3000 .8348 4000 .7924 5000 .7550			009	°08	1000	120°	140°	100		
5. 5. 5.	0200	1 1971	1.3078	1.4227	2.2381	2.3835	2.5399	2.7054	2.8849	3.0725
9. 9. 9.	0000.1	11104	1 9168	1.3196	1.4257	2.184	2.326	2.476	2.639	2.808
	1.0248	1.1104	1 1411	1.2340	1.3283	2.018	2.147	2.283	2.433	2.580
	9644	6160.1	1 0769	1.1608	1.2451	1.877	1.995	2.120	2.257	2.397
	2616.	0400	1 0192	1.0971	1.1739	1.226	1.866	1.982	2.106	2.235
_	.8047	0046.	6090	1 0419	1.1123	1.147	1.755	1.861	1.975	2.092
_	.8235	cc68.	Zene.	9000	1 0590	1.077	1.178	1.755	1.861	1.968
6000	.7865	.8547	.9240	0766.			,	1 669	1 758	1.857
7000 .6922	.7538	.8183	.8844	.9495	1.0118	1.017	1.112	1.002		ì
8000	.7243	.7862	.8492	.9100	3696	0.964	1.053	1.578	1.667	1.758
	0869	.7569	.8167	.8758	.9320	0.917	1.002	1.505	1.588	1.670
	.6741	.7305	.7878	.8443	9868	0.875	0.956	1.033	1.517	1.593
•	.6528	0707.	.7618	.8163	0698	0.841	0.919	0.991	1.455	1.525
	.6332	.6854	.7381	.7908	.8425	0.810	0.885	0.954	1.401	1.464

description of the capillary and the method of filling it will be found under potassium. Seven runs were made with the sodium in glass, with several different capillaries. These runs were at 134.0°, on both solid and liquid, at 143.6° on the liquid only, at 163.1° on the liquid only, at 165.0° on both liquid and solid, and at 171.8°, 197.1° and 198.1° on the liquid only. In addition, readings were made at atmospheric pressure from which the change of resistance on melting and the temperature coefficient of resistance of the liquid could be obtained. These runs were of varying degrees of excellence. Those at 165° and 197° showed zero shifts of only 0.5% and 0.3%, and were given the greatest weight in computing the resistance of the solid. In general the observed points lay very smoothly, and there was little difference between the results with increasing and decreasing pressure, indicating little direct effect due to the constraint exerted by the walls of the capillary.

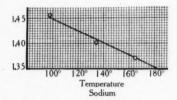


FIGURE 3. The ratio of the resistance of liquid to solid sodium as a function of temperature along the melting curve.

The ratio of resistance of liquid to solid was observed at three temperatures; the observed points are shown in Figure 3. The ratio decreases somewhat with increasing pressure and temperature along the melting curve. In reducing the observed values to smoothness, it was assumed that the ratio varies linearly with temperature, and is given by the line shown in the figure.

The values of resistance as a function of pressure and temperature from 0° to 200° and to 12000 kg. are shown in Table III. This table falls into two parts; the first part, including the values through 100°, are relative values of the "observed" resistance, being derived from measurements on the bare wire. Above 100° the values listed are relative values of the specific resistance, the observations having been made on the sodium in a glass capillary, and corrections applied for the compressibility and thermal expansion of the glass. For the

linear expansion the value 0.058 was assumed, and for the cubic compressibility Amagat's figure 2.2×10^{-6} , with his temperature coefficient of compressibility of 10% for 100°. In order to reduce the part of the table below 100° to relative specific resistances or that above 100° to relative "observed" resistances, it would have been necessary to have known the compressibility of sodium over this range of pressures and temperatures, and this has not yet been determined experimentally. From the differences of the pressure coefficients in the two parts of the table, however, it is possible to get some idea of the magnitude of the compressibility. Thus it will be found that the mean coefficient of "observed" resistance between 5000 and 12000 kg. at 100° becomes consistent with the mean coefficient of specific resistance over the same range if the compressibility is 0.00002. Richards found for the initial compressibility at 20° the value 0.000015. The difference between these two values does not mean an impossibly large temperature effect.

In Figure 4 the isothermals of resistance against pressure have been drawn for a number of temperatures. The values are taken from the table and have the same discontinuity at 100° as the values of the table. In fact, this discontinuity is quite evident in the figure. The change of resistance with pressure is seen to be large, larger than for any other metal which I have measured except potassium. Under 12000 kg. the change of resistance of the solid is of the order of 40% of the initial resistance. The mean coefficient of the liquid is larger, the decrement being about 50% for the same pressure range. The initial coefficient of the liquid varies little with temperature, but the initial coefficient of the solid increases markedly with rising temperature.

The pressure coefficient of resistance of sodium has not been previously measured, so there are no other values for comparison, but other observers have measured the temperature coefficient of solid and liquid and the ratio of resistance of liquid to solid at atmospheric pressure. The values of Northrup and Bernini for the coefficient of the solid have been already quoted. It is to be noticed that the values of Northrup and Bernini are for the specific resistance, since their materials were enclosed in a rigid container, whereas my coefficient is of the "observed" resistance, and was obtained on the bare solid. The coefficient of specific resistance is greater than that of "observed" resistance by the linear expansion. Taking as the linear expansion of sodium 0.000069, my value of the coefficient of the "observed" resistance would give 0.00552 for the coefficient of the specific resistance. This value is seen to be much higher than that

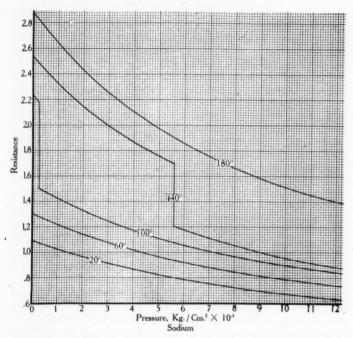


FIGURE 4. Relative resistances of sodium at constant temperature as a function of pressure.

of Bernini, and appreciably higher than that of Northrup. Doubtless the freedom from constraint of the bare wire is in large part responsible. As the solid sodium expands in the glass container it will exert a pressure on the walls, which will have the effect of decreasing the resistance, and making the temperature coefficient appear too low.

For the temperature coefficient of the liquid, Bernini 6 found between 100° and 110° 0.00279 of the resistance at 100° . Northrup's 5 mean value between 100° and 140° is 0.00330 of the resistance at 100° . My mean value between 100° and 120° is 0.00325, slightly lower than the value of Northrup. It is not yet established whether the purer liquid metal usually has a higher temperature coefficient than the impurer or not.

For the ratio of the resistance of liquid to that of solid at the melting point Bernini found 1.337, and Northrup 1.44. The value which I found above was 1.451, in good agreement with that of Northrup. The agreement of my high pressure values with that found at atmospheric pressure makes it probable that in my work the formation of cavities did not cause any essential error at atmospheric pressure.

It will be noticed that throughout, my values are considerably closer to those of Northrup than Bernini. It is probable that in spite of his efforts, Bernini did not succeed in eliminating the effect of cavities, or that there was some other source of consistent error.

Potassium. Material from the same lot was used as that used previously for the measurements of the coordinates of the melting curve. The purity was high, as shown by the sharpness of freezing. Resistance measurements under pressure were made on both the liquid and the solid. The mechanical softness of potassium, and its much greater chemical activity made it infeasible to use the solid in the form of bare wire, as had been possible with sodium and lithium. metal had to be contained, therefore, in a glass capillary. This is to be regretted, but its much greater softness makes any error introduced by the restraining action of the glass much less than in the case of the other metals. Special examination was made of the magnitude of the error introduced in this way by measuring the difference between the resistance under increasing and decreasing pressure at 28°. Very noticeable differences between the ascending and descending curves were found, corresponding to a maximum difference of mean pressure in the metal and the surrounding liquid of 100 kg. The maximum discrepancy occurred at the highest pressure, where it would be expected that the viscosity of the metal would be the The pressure difference of 100 kg, was estimated from the differences of resistance, assuming that the stresses in the metal had the same effect on resistance as a hydrostatic pressure. Of course there actually were stresses in the metal of a shearing nature, and it is exceedingly unlikely that the effect of such stresses is equivalent to a hydrostatic pressure, so that it is probable that the glass capillary was called on to support a stress difference of considerably more than The mean of readings with ascending and descending pressure were taken as the correct value. There were, however, considerable irregularities, doubtless due to the irregular response of the glass capillary to the heterogeneous strains in it. At higher temperatures the differences between the readings with ascending and descending pressure became much less than at 28°, as one would expect, but it was

evident that some of the irregularities remained at all temperatures. In view of the probably much greater magnitude of the effect at still lower temperatures, no readings were attempted at temperatures lower than 28°.

The capillary containing the potassium was in the form of a U, with open cups at the two ends. Into each cup, two fine platinum wires were sealed for the current and potential leads, and measurements were made by the potentiometer method. The capillary was filled by melting the potassium into it in high vacuum. The filling was accomplished by sealing one of the cups, and connecting to the other cup a succession of bulbs communicating with each other through narrow necks. The potassium was placed in the most remote of the bulbs, and the apparatus was exhausted with a diffusion pump, heating the bulbs and capillary to remove occluded gases. The glass was now sealed off from the pump, and the melted potassium run in succession from one bulb to the next. In this way the scum of oxide was removed. Previous work had shown that further purification of this particular specimen of potassium, as by distilling, was superfluous. When the melted potassium reached the cup of the capillary, into which it could not enter because of capillary action, illuminating gas was admitted to the farther bulb, driving the melted potassium before it and thus completely filling the capillary. The seal of the other cup was now broken, and the capillary mounted as soon as possible in the pressure apparatus under Nujol, the open ends of the capillaries being protected from oxidation with Nujol and paraffine paste during mounting.

Five runs were made, with two capillaries. The first filling gave measurements of the resistance of the solid alone at 28.6° and 54.2°. The second filling was used at higher temperatures, 95.7°, 132.2° and 167.0°, and gave measurements on both solid and liquid. For the second set of runs a special apparatus had to be used by which the insulating plug was kept cold in a third cylinder. This was first used in the measurements on liquid bismuth, and will be found described under that metal. The same apparatus was also used in the high temperature measurements on lithium and sodium. In addition to the pressure runs, the same fillings of the capillaries were used to give the temperature coefficient of resistance by varying the temperature

at atmospheric pressure.

The resistances as measured were smoothed to uniform temperature and pressure intervals, choosing a temperature interval of 35° as being closest to the greatest number of the actual readings. In this smooth-

ing the irregularities introduced by the glass capillary were apparent. The individual readings seldom showed irregularities of much more than the sensitiveness of the measurements, but there were consistent departures between readings with increasing and decreasing pressure, and consequent uncertainty as to the correct result. Sometimes an adjustment of as much as 2% in the total resistance was necessary to bring the runs for different temperatures into smooth register with each other. Because of the extreme largeness of the coefficient, a change of 2% in the resistance itself usually means a much smaller percentage change in the decrement of resistance. Since it was the decrement which was measured, the actual measured quantities

TABLE IV.
RESISTANCE OF POTASSIUM.

Pressure kg/cm ²	25°	60°	95°	130°	165°
0	1.128	1.307	2.387	2.724	3.040
1000	.941	1.079	1.911	2.222	2.568
2000	.799	.911	1.586	1.842	2.176
3000	.692	.786	.880	1.567	1.853
4000	.615	.696	.777	1.346	1.586
5000	.554	.623	.693	1.183	1.374
6000	.503	.563	.624	.685	1.195
7000	. 458	.511	.564	.618	1.050
8000	. 420	. 464	.508	.551	.928
9000	.387	. 425	. 463	.500	. 829
10000	.358	.389	.420	.450	. 481
11000	.333	.358	.383	. 407	. 432
12000	.310	.330	.350	.369	.389

seldom had to be adjusted by as much as 2%. In making the adjustments, the observed temperature coefficients of both solid and liquid at atmospheric pressure was accepted as most probably correct and retained with only immaterial smoothing. Also the observed change of resistance on passing from the liquid to the solid at various temperatures was accepted as essentially correct. With these as fixed data in the table of resistances, the other measured values for the decrement of resistance were adjusted to smoothness with as little change as possible.

The resistances as thus smoothed are shown in Table IV. The

values tabulated are relative values of the specific resistance, taking as unity the resistance of the solid at atmospheric pressure at 0°. The observed values have been corrected for the expansion and compressi-

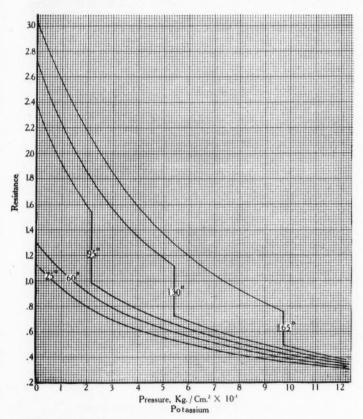


Figure 5. Relative resistances of potassium at several constant temperatures as a function of pressure.

bility of the glass, assuming for the linear expansion 0.0_57 , and for the linear compressibility 0.0_68 . The corrections so introduced are much smaller than usual, because of the very large pressure and temperature

coefficients of this substance. The correction for the thermal expansion of the glass is perceptible as a change of one unit in the last figure in only one part of the table, and the maximum correction for the compressibility is 0.96% of the corresponding resistance. It is to be noticed that the table contains relative specific resistances, and not relative "observed" resistances, as is the case for all metals which are measured in wire form. It is also to be noticed that the table contains the resistances of both solid and liquid; the domain of the solid is separated from that of the liquid by a heavy line.

The data of the table have been plotted in Figure 5. The first and most striking result shown by the table and the figure is the great magnitude of the effect; it is not equalled by any other metal, and is exceeded only by black phosphorus among the substances which I have measured. At 25° the resistance of the solid at 12000 kg. is only 27.5% of its resistance at atmospheric pressure. At the higher temperatures, where change of phase occurs, the resistance at 12000 may be as little as 13% of the atmospheric value. At the melting temperature at atmospheric pressure the coefficient of the liquid is greater than that of the solid, but the coefficient of the liquids shows a quite marked decrease with rising temperature.

TABLE V.
POTASSIUM.
Relative Values of Specific Resistance on the Melting Curve.

Temperature	Pressure	e Resistance			
Centigrade	kg/cm ⁹	Liquid	Solid		
62.5°	0	2.059	1.320		
95.0°	2200	1.540	0.990		
130.0°	5430	1.128	0.728		
165.0°	9710	0.772	0.498		

In Table V are shown the resistances, also in terms of the resistance of the solid at 0° at atmospheric pressure as unity, at the melting points. Within the limits of error, the ratio of specific resistance of the liquid to that of the solid at the melting point is nearly independent of the pressure and temperature of melting. The experimental

values found were 1.664 and 1.56 at 62.5° and 0 kg., 1.493 at 95.7° and 2260 kg., 1.550 at 132.2° and 5650 kg., and 1.550 at 167.0° and 10000 kg. The higher of the two values at atmospheric pressure was not satisfactory because the capillary was not filled as well as usual, there being obviously minute cavities between the surface of the metal and the glass, and that result was accordingly discarded. The remaining results show that the ratio is almost exactly constant, and in computing the tables the following values were used; 1.56 at 0 kg. 1.555 at

2200 kg., 1.550 at 5430 kg., and 1.550 at 9710 kg.

The value for the ratio of the resistance of liquid to that of solid at atmospheric pressure may be compared with that of other observers. Bernini 7 has found 1.392, and Northrup 5 1.53. It is to be seen that my value agrees much better with that of Northrup. This entire question of the ratio of the resistance of the liquid to that of the solid is still in a most unsatisfactory state experimentally, and results by different observers disagree by much more than can be accounted for by errors of measurement or by impurity of the materials. All values with which I am acquainted, both for potassium and other metals as well, have been obtained from measurements of the liquid in a glass capillary, and from measurements of the solid in the same capillary after freezing. The resistance of the solid is without doubt likely to be largely in error because of strains and because of cavities formed during freezing. Matthiesen,8 in his early work, found discrepancies in measurements of the resistances of the solid of as much as 5\% which he traced to this cause. What is more, after the solid has once been formed, and is again melted to the liquid, there may be cavities between the surface of the liquid and the glass. Bernini has found large discrepancies in the resistance of the liquid due to this cause. Furthermore, in most experiments, there has been a film of oil between the surface of the metal and the glass; irregular capillary effects in this film will introduce error. Much of the previous work should be repeated with increased precautions. Measurements on the liquid should be made with a capillary completely filled in vacuum, and the liquid should not be allowed to freeze. The specific resistance of the solid should be obtained from independent measurements of the bare metal, preferably extruded to ensure complete freedom from cavities. Measurements on both solid and liquid should be made over a wide enough temperature range to allow unquestionable extrapolation to the melting point. No measurements should be given much confidence which show premature rounding of the corners of the melting curve. It can now be stated with confidence that all such premature

rounding is due to impurity; in the early days of this kind of measurement there was room for honest question whether the absolutely pure substance would show premature rounding or not.

While it cannot be claimed that the measurements above meet all these requirements, it is evident that any error from cavities must be negligible when freezing takes place under thousands of atmospheres, and as far as purity goes, the potassium used above never showed any preliminary rounding, thus bearing out the observations on the same material on the melting curve. The melting of Bernini's sample was not abrupt, and took place at 62.04°, nearly 0.5° below that of mine. Northrup records the value 63.5° for the melting point of his specimen; this is so high that it seems that it must be due to errors in temperature measurement.

The value which I found for the temperature coefficient of resistance at atmospheric pressure is considerably lower than that of either Bernini or Northrup. The first found 0.00601 between 0° and 50°, and the latter found 0.0058, in terms of the resistance at 0°C. between 20° and 50°. I found the relation to be linear, and the value of the coefficient, corrected for the expansion of the glass, 0.00512 between 0° and 50°. My value for the liquid is, on the other hand, larger than that of Bernini. I find for the mean coefficient between 95° and 130° 0.00403 of the resistance at 95°, and Bernini gives between 90° and 100° 0.00358 of the value at 95°. Northrup's value, reduced to fractional parts of the resistance at 95°, is 0.00342.

In using the Table, caution should be employed not to force it beyond its accuracy. In particular, too much importance should not be attached to the variation of the differences with temperature. If at any time in theoretical work it should be important to know exactly the variations of pressure and temperature coefficients with pressure and temperature for small ranges of pressure, this work should be repeated with apparatus capable of measuring pressures with greater sensitiveness, and the pressures should not be pushed so high as to introduce irregularities in the glass. In this work the smallest pressure steps were 1000 kg., and no readings were made between 0 and 1000 kg. Where the changes are so large in an interval of 1000 kg. it is entirely possible that some essential detail of behavior may have been overlooked, or smoothed out in constructing the Table.

Magnesium. In the previous paper on the resistance of metals under pressure it was possible to give only very rough values for the pressure coefficient of magnesium. Difficulty was previously found in making good connections because of the impossibility of soldering

magnesium and because of the very high resistance of the film of oxide on the surface. With a potentiometer method of measuring resistance, however, this was no longer a difficulty, and accordingly the attempt

was made to get more accurate values.

Measurements were made with two samples of magnesium. first was from the same piece as that on which measurements of resistance and thermal e.m.f. have been already published, and was a contiguous length from the same spool as the e.m.f. sample. It was originally obtained from Eimer and Amend, of commercial quality. The method of manufacture of magnesium, however, is such that impurities are not likely to get into it, and it is a matter of experience that commercial magnesium is of higher absolute purity than most commercial metals. The second sample I owe to the kindness of Dr. MacKay of the Research Laboratory of the General Electric Co. It had been especially purified by him by distillation in vacuum. was extruded hot to wire of about 0.020 inches diameter, the same in dimensions as the other specimen. Both specimens were mounted in the same way for the measurements, by winding bare on a bone core. Contact was made with spring clips. The resistance at the contacts was so high that error might be introduced because of fluctuations of the potentiometer current, unless the precaution were taken to brighten the wire with sandpaper immediately under the clips just before assembling the apparatus. With this precaution no trouble was experienced from contact resistance.

The measurements on the first sample of magnesium were made just after the apparatus had been constructed, and before all points in the best handling of it had been settled, so that there were a number of incomplete runs. In all, there were ten runs on this sample, five of them complete. The incomplete runs were given due weight in the final results. The maximum deviation of the individual readings from regularity was of the order of 1%. It will not pay to reproduce the results in detail, because this sample was presumably less pure

than the second, and the results are somewhat different.

Three runs were made on the second and purer sample, at 0°, 51° and 95°, after three preliminary applications of 3000 kg. at room temperature to season. The results were smoothed and a Table constructed in the regular way. The readings ran regularly. At 0° the zero displacement after the run was 1.6% of the total effect, at 51° it was 1.2%, and at 95° 0.85%. These displacements are also essentially the same as the maximum departures from a smooth curve of any of the other observed points. The results are exhibited in Table VI and Figure 6

TABLE VI.
MAGNESIUM.

Temp °C.	Resistance	P. At 0 kg.	ressure Coeffici	Average 0-12000	Maximum Deviation from Linearity	Pressure of Maximum Deviation
0°	1.0000	-0.0 ₆ 477	-0.0,311	-0.0 ₅ 4080	.00238	6500
50	1.1975	462	348	4065	196	5900
100	1.3900	473	341	4018	283	5600

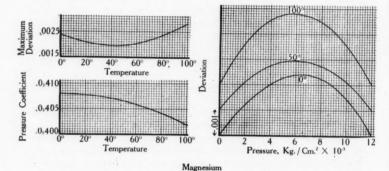


Figure 6. Results for the measured resistance of magnesium. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

in the same way as the results of the previous paper. The average pressure coefficient decreased with rising temperature, which is unusual. The relation between resistance and pressure departs from linearity in the usual direction, but it is unusual that the relation is more nearly linear at 50° than at either 0° or 100°. The pressure of maximum departure from linearity moves programively towards lower values at higher temperatures.

It is interesting to compare these values with those found for the first and presumably less pure sample. The temperature coefficient of the first sample was 0.00412, against 0.00390 for the second, and

the relation between temperature and resistance was linear between 0° and 100°. Here we have the unusual case of the presumably purer substance with a smaller temperature coefficient. Recent observations of Holborn 9 make it likely, however, that the behavior of aluminum is similar, and it is not surprising if the behavior of magnesium and aluminum should be the same. The average pressure coefficients of the first sample between 0 and 12000 kg, were -0.05446, 441, and 436 at 0°, 50°, and 100° respectively. This is seen to be about 10% higher than that of the second sample. The two samples agree, however, in having a coefficient which decreases with rising temperature. The maximum departures from linearity of the impurer sample were also nearly the same as for the purer, the maximum deviations being 0.0023, 0.0026, and 0.0029 at the three temperatures respectively. The deviations from linearity of the first sample were symmetrical with respect to pressure, in each case the relation between pressure and resistance being representable by a second degree equation, and the pressure of maximum deviation being at 6000 kg. The first sample differs from the second in not showing a closer approach to linearity at 50° than at the other two temperatures.

These new and more accurate results differ considerably from the rough value given for the first sample; it was stated in the previous paper that the average coefficient for the first sample was probably

-0.0555.

CALCIUM. This material was obtained from the Research Laboratory of the General Electric Co. through the kindness of Dr. Langmuir. An analysis by Mr. N. S. Drake by the method of differences showed not more than 0.1% total impurity, the error of the measurements being 0.1%. Qualitative analysis showed no detectible impurity except a trace of iron, too small to determine quantitatively.

The calcium was furnished in the form of a solid ingot about 1 inch in diameter. Pieces of the appropriate size were cut from it with a hack saw, and were formed into wire 0.013 inches in diameter by extrusion through a steel die. An extrusion pressure of the order of 10000 kg per cm² was required. A phenomenon shown to a more or less pronounced degree by all metals during extrusion was particularly prominent with calcium. If the extrusion pressure is pushed too high, or sometimes for no apparent reason, the wire will suddenly break and the metal spit out of the extrusion block in long gulps or small pieces. This spitting forth reaches explosive violence in the case of calcium, and the fine dust into which the issuing wire breaks takes fire spon-

taneously. The explosive sound, the flash of fire and the pungent smoke are likely to be rather terrifying on first experience. For nearly all metals the effect can be greatly reduced by a proper design of the die; the best shape of the die varies from metal to metal.

In spite of the satisfactoriness of the chemical analysis of this sample, it must be recognized that there may perhaps have been in this specimen minute impurities which possibly may have exerted an appreciable effect on the electrical properties. It has been the experience of the General Electric Co. that different samples of calcium, with no perceptible chemical difference, offer very different resistances to extrusion. The effect may not be chemical, and its explanation is entirely obscure. There is no way of knowing whether the specimens difficult of extrusion are more or less likely to be impure, and no connection seems to have been looked for between extrusion and electrical characteristics. The specimen used by me was difficult of extrusion; we cannot now make any use of this fact, but if in the future the cause of the variations should be found, it is well to have the characteristics of this specimen recorded.

Temperature had to be raised to 400° or higher for successful extrusion. Although extrusion would take place at lower temperatures. the wire so formed was brittle, and could be handled only with difficulty. In any event, the best wire that could be formed had to be handled with care. It broke if bent more than once at a sharp angle, and was entirely different in its properties from sodium. Extrusion took place directly into the air, but as the wire exuded from the die. it was wound immediately onto a spool covered with a protecting paste of Nujol and paraffine. Chemical action by the air is much slower than in the case of sodium and lithium, but is no less complete, the wire eventually crumbling away into dust after standing several weeks. Even the Nujol and paraffine does not act as a complete protection, but there is either direct action or else slow diffusion of the air through the protective coating. In order to avoid error from this effect, the wire must be mounted in the pressure apparatus and measurements made as soon after extrusion as possible, while it is still Unless this procedure is followed effects from the high resistance of the surface film are much more troublesome than for any other metal I have tried, not excepting magnesium. With fresh wire, however, such effects become vanishingly small with proper manipulation. The contact resistance may always jump spasmodically under increases of pressure, but with fresh wire the contact can always be sufficiently restored by the momentary passage of a current from a small magneto.

The wire was wound as usual bare on a bone core, and connections made with spring clips, using a protective coating of gold foil at the

point of contact. Runs were made on two samples and at five temperatures, 0°, 25°, 50°, 75° and 96°. The runs on the first sample were terminated by the failure of the insulation of the three-terminal plug. The transmitting medium was Nujol and petroleum ether. Chemical action was never entirely absent, but as in the case of sodium, it was mostly confined to low pressures. It increases rapidly with rising temperature, and at 96° was so rapid that 1500 kg, was the lowest pressure at which readings were attempted. Unlike sodium and lithium, calcium shows pronounced seasoning effects of pressure, and the runs at 25° and 75°, which were those of the initial application of pressure to the two samples respectively, were much less regular than the subsequent runs. Because of the necessity of obtaining readings rapidly because of chemical action, preliminary seasoning applications of pressure were omitted, and the initial runs were included in the final results. At 25° the total zero shift (initial application) was 4.2% of the total pressure effect; at 0° 0.5%; at 50° 3.9%; at 75° (initial application) 6.9%; and at 96° (zero taken from 1500 kg.) 3.3%. At 25° and 75° the individual points lie very closely on two smooth curves, different for increasing and decreasing pressure. The incomplete seasoning shows itself in a sequence of readings like that of an open hysteresis loop. The open end of this loop at atmospheric pressure has the width given above by the zero displacements. At the other temperatures the readings also show a tendency to hysteresis effects, but the departure from the mean is much less. At 0° the maximum departure of any single point from the smooth curve representing the mean of the points with increasing and decreasing pressure is 1.2% of the total effect; at 50°, 1.5%; and at 96°, 1.5%.

The temperature coefficient of resistance at atmospheric pressure was determined by the same method and at the same time as the readings for sodium and lithium. The "observed" resistances, which are the mean of points with ascending and descending temperature, at four temperatures (0°, 25°, 50°, and 75°) all lie within the limits of error (one part in 7000) on a second degree curve. The total shift of the zero during the run, presumably due to chemical action, was 1.6% of the total temperature effect. The value given in the table for the resistance at 100° was obtained from the second degree curve by extrapolation. The mean coefficient between 0° and 100° determined in this way is 0.003327.

The temperature coefficient of resistance of Calcium at atmospheric pressure has been previously measured by Northrup, ¹¹ who found between 0° and 100° the value 0.00246, and by Swisher, ¹⁰ who found the relation between temperature and resistance to be linear between 0° and 600°, and the coefficient to be 0.00364 of the value at 0°. An examination of Swisher's results shows that there were considerable irregularities, and that within his limits of error it is not possible to say whether his coefficient between 0° and 100° is greater or less than my value above. The low value of Northrup is probably due to impurity in his sample.

In smoothing the experimental results for the most probable final values, the usual procedure was followed. The results at each temperature were first smoothed independently, and then readjusted so as to give smooth temperature differences. The effect of insufficient seasoning in the runs at 25° and 75° was shown by the greater readjustments necessary at these temperatures. The maximum readjustment necessary was 0.0% at 0° , 4.6% at 25° , 1.4% at 50° , 1.8% at 75° , and 0.4% at 96° .

TABLE VII. CALCIUM.

Pressure kg/cm ²	00	25°	Resistance 50°	75°	100°
0	1.0000	1.0748	1.1552	1.2402	1.3327
1000	1.0107	1.0859	1.1668	1.2522	1.3454
2000	1.0217	1.0974	1.1789	1.2651	1.3589
3000	1.0330	1.1092	1.1912	1.2780	1.3725
4000	1.0447	1.1213	1.2039	1.2914	1.3865
5000	1.0569	1.1340	1.2171	1.3051	1.4008
6000	1.0696	1.1473	1.2309	1.3193	1.4157
7000	1.0827	1.1609	1.2451	1.3341	1.4311
8000	1.0963	1.1751	1.2599	1.3495	1.4470
9000	1.1103	1.1896	1.2749	1.3650	1.4631
10000	1.1247	1.2045	1.2903	1.3810	1.4797
11000	1.1396	1.2200	1.3064	1.3976	1.4969
12000	1.1550	1.2360	1.3229	1.4147	1.5146
Average					
Coefficient 0-12000 kg.	+0.041292	+0.01242	+0.041210	+0.041172	+0.041137

The final results for resistance as a function of pressure and temperature are given in Table VII. The striking and unexpected result, as in the case of lithium, is the positive coefficient. The coefficient is greatest at the lowest temperature, having the average value +0.041292 at 0°. Both the instantaneous and the average coefficient increase with rising pressure. In both these particulars the behavior is much like that of bismuth. The absolute value of the coefficient is of the order of half that of bismuth.

Bismuth is abnormal in so many other respects than its pressure coefficient, that it seemed of interest to find whether calcium has the same sort of abnormalities. The large increase of resistance of bismuth in a magnetic field is one of the well known abnormal effects. I tried the effect of a field of approximately 27000 Gauss on the resistance of a coil of calcium, the wires of the coil being everywhere at right angles to the field, and found a decrease of resistance of only 1/1600. It is evident, therefore, that any parallelism between the conduction mechanisms of calcium and bismuth cannot be very complete. A more exhaustive investigation of the various properties of calcium than has yet been made seems well worth while.

In a previous paper it has been shown that the abnormal positive pressure coefficients of resistance of bismuth and antimony are associated with values of the thermal expansion abnormal as compared with the other properties. The same comparison for calcium appeared of interest, but the thermal expansion of calcium has apparently not been previously measured, and I accordingly made special measure-

ments of it.

The thermal expansion was determined by ordinary methods, using a glass dilatometer. The calcium was the same specimen as that from which the resistance sample was cut. It was turned over its entire surface in the lathe, and finished to a cylinder about 6 cm. long and 20 cm³ volume. The surface was smooth, without blowholes. In the glass dilatometer the calcium was surrounded with Nujol. The calcium and Nujol had been previously heated together in another vessel to 100° to avoid as far as possible chemical action during the dilatometer readings. Discoloration of the surface of the calcium by this preliminary heating was very slight. Air bubbles in the dilatometer were avoided by filling in vacuum. The Nujol is so viscous that without special precaution error may be introduced by sticking of the Nujol to the walls of the capillary. This error was avoided by heating the capillary before the readings with a small gas flame, and by making readings with increasing temperature. A pre-

liminary attempt was made to avoid the error by using petroleum ether as the medium, which is very much more fluid than the Nujol. This was unsuccessful because of chemical action between the petroleum ether and the calcium. Readings of the expansion of the calcium and Nujol were made at 0°, 25°, and 50°. At 50° a very few exceedingly minute bubbles appeared, probably the beginning of chemical action. Accordingly the readings at 50° were discarded. The auxiliary data needed in the computation were obtained from the dilatations when the dilatometer was entirely filled with Nujol and with mercury respectively. The volumes of the dilatometer and the capillary were obtained by weighing the mercury required to fill them. The bore of the capillary was calibrated for uniformity by conventional methods. The density of the calcium was obtained by weighing it in air and under Nujol. The densities given are corrected for vacuum.

The following values were obtained for calcium:

Density at 21° 1.5563 Coefficient of volume expansion, 0° to 21°, 0.000075.

The values for Nujol were obtained incidentally and are recorded.

Density at 21° 0.8786 Coefficient of volume expansion, 0° to 21°, 0.000717.

STRONTIUM. Particular interest attaches to this metal because of the fact that it is underneath calcium in the periodic table, and calcium is unusual in having a positive coefficient. The material I owe to Dr. G. E. Glascock, who very kindly placed at my disposal some of the material whose preparation and properties he has described. 12 The metal was prepared by the electrolysis of the fused salts. It was in the form of fused nodules of sometimes two or three cubic centimeters volume, and had been kept since preparation under kerosene. Some sort of action had taken place between the metal and the kerosene. under which most of the kerosene disappeared, and the metal became coated with a fine gray powder. The action of calcium on kerosene I have found to be very similar. On scraping off the grav powder, the coherent metal is found underneath. On cutting into the cleaned nodules with a cold chisel, slag-like inclusions are sometimes found. Lithium prepared by electrolysis shows the same appearance. By careful selection it was possible to find pieces large enough free from these inclusions.

The measurements were made on the metal in the form of wire approximately 0.020 inches in diameter, formed by extrusion from one

of the selected pieces of clear metal. The extrusion is considerably easier than that of calcium, and may be successfully performed at a temperature of 230°. At room temperature the metal spits out of the die in small pieces. The wire is fairly soft and pliable and can be bent to a radius of perhaps ten times the diameter of the wire, but it is quite different in mechanical properties from the alkali metals, such as sodium, and shows brittleness if too sharp a bend is attempted.

Previous measurements on the electrical properties of strontium seem to have been published only by Matthiesen.8 He extruded the metal to wire in much the same way as above. He gives for the specific resistance at 20° the value 25×10^{-6} ohms per cm. cube. I found at 0° for my specimen the value 30.7×10^{-6} . This specimen is presumably considerably purer than Matthiesen's, and this value would seem to be preferred. Matthiesen did not attempt to measure the temperature coefficient of resistance, probably because of resistance of the contacts. He did not use a potentiometer method, but had to correct as best he could for the resistance of his leads and contacts. With a potentiometer method as used here, there is no such difficulty. There is difficulty, however, in the chemical action accompanying changes of temperature, which produces permanent changes of resistance. Error from this effect was avoided by the same procedure as that used previously for the alkali metals. Four thermostated baths were kept simultaneously in operation, and the specimen transferred rapidly from one to another. The bare wire was immersed in a glass tube of Nujol for the measurements, the Nujol having been previously heated with sodium to remove all moisture and exhaust as far as possible all tendency to chemical action. There nevertheless seems to have been some specific action between the oil and the strontium. About fifteen minutes were required for the attainment of temperature equilibrium after the wire had been transferred from one bath to the next. Readings were made with ascending and descending temperature between 0° and 96°, starting with 0° and ending with 0°. The mean of the ascending and descending readings was taken as the true effect. The permanent change of zero after the excursion was 12% of the maximum effect. The mean coefficient between 0° and 100° found from these readings was 0.00383. The effect is not quite linear with temperature, but the change becomes more rapid at the higher temperatures, as is normal.

The value of the temperature coefficient is quite normal for pure metals, and in the absence of further information, makes it probable that this material was of satisfactory purity. It is not possible to obtain the analysis from the paper of Glascock, because the products of his separate electrolyses were not always of the same purity, and the different batches were indiscriminately mixed in the material as supplied to me. The least pure of any of the specimens of Glascock

had about 2\% impurity, and the best about 0.15\%.

Pressure measurements were made in the regular way with the potentiometer. The wire was used bare, and the connections were made with spring clips. The resistance of the contacts increased during the runs, and sometimes became troublesomely large; it could then be reduced by passing a high tension current from a small magneto through the contacts. The wire was seasoned by a preliminary application of 3000 kg. at room temperature; there was no perceptible change of zero after this application. Three runs were made; at 0°, 50.5°, and 97°. At the highest temperature the zero of pressure was taken as 500 kg, in order to prevent chemical action, and the value at atmospheric pressure obtained by extrapolation. Considering the chemical activity of this material the readings showed a gratifying regularity. At 0° there was a permanent change of zero of 1.8% of the total effect, at 50° the change was 0.3%, and at 97° 2.1%. The maximum departure of any of the other points from the smooth curve was 1.6% at 0°, 1.2% at 50°, and except for one bad point, 1.5% at 97°. The observed resistances were smoothed and a table constructed for the resistance at regular intervals of pressure and temperature in the regular way.

The results are shown in Table VIII and Figure 7. The resistance increases under pressure, the same as for calcium. The increase is furthermore very large; it is five times as large as that of calcium, and three times that of bismuth, and is the largest positive coefficient yet found. The behavior is in other respects like that of other metals with a positive coefficient. When the resistance is plotted against pressure, the curve is concave upwards, the change becoming more rapid at the higher pressures. The coefficient becomes markedly smaller at the higher temperatures. The instantaneous coefficient becomes smaller at the higher pressures; this was not the case for bismuth. One may be puzzled at first by the Table which shows a smaller instantaneous coefficient at both 0 kg, and 12000 kg, than the average coefficient between 0 and 12000. The reason for this is that the instantaneous coefficient is calculated in terms of the resistance at the pressure in question, which becomes rapidly greater at the higher pressures, whereas the average coefficient is calculated in terms of the initial resistance at 0 kg. The resistance shows a regular drift

TABLE VIII.
STRONTIUM.

Pressure kg/cm ²	Resistance 0° 50° 100°				
0	1.0000	1.1768	1.3828		
1000	1.0516	1.2320	1.4341		
2000	1.1058	1.2906	1.4908		
3000	1.1622	1.3519	1.5539		
4000	1.2220	1.4166	1.6214		
5000	1.2850	1.4842	1.6936		
6000	1.3508	1.5544	1.7712		
7000	1.4196	1.6280	1.8527		
8000	1.4916	1.7051	1.9381		
9000	1.5670	1.7852	2.0272		
10000	1.6462	1.8684	2.1198		
11000	1.7290	1.9550	2.2157		
12000	1.8160	2.0446	2.3144		
Average Coefficient 0-12000 kg.	+0.046800	+0.046146	+0.045614		
Coefficient at 0 kg.	0.04502	0.04456	0.04351		
Coefficient at 12000 kg.	0.04492	0.04451	0.04432		

with increasing temperature. At 0° the third derivative of the resistance as a function of pressure is positive, at 50° it is zero, and at 100° it is negative.

Mercury. I have already published results for the resistance of liquid mercury as a function of pressure and temperature, 13 but I have now found it possible to considerably extend the range of the previous work. Previous work on the liquid was between 0° and 50° and to 6500 kg., and a few very rough qualitative results were obtained for the solid. The results for the liquid have now been extended over the temperature range 0° to 100° and over the pressure range to 12000 kg. In addition, the resistance of the solid has been accurately meas-

ured at 0° between the solidifying pressure (7640) and 12000 kg., and the change of resistance on solidifying at 0° has been also determined.

The liquid was measured with the Carey Foster bridge, by the same method used for most metals in the form of fine wire. The mercury was contained in a U-shaped capillary, and connections were made to

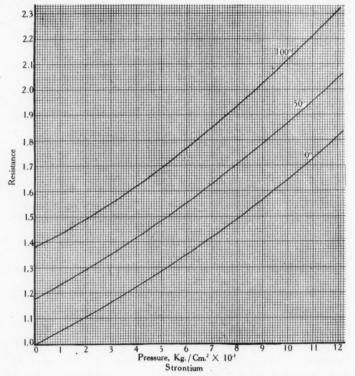


FIGURE 7. Relative resistances of strontium at several constant temperatures as a function of pressure.

the mercury by amalgamated copper wires dipping into cups at the upper ends of the U. The resistance was about 10 ohms. The capillary was of Jena glass No. 3880a, the same grade of glass as that used in the previous work. This particular capillary was blown in 1907,

and had been last used in 1911, when it had been exposed to the freezing pressure of mercury at 0°, and had since been resting in a dust proof container. The measurements on the liquid recorded here were made in 1917. The technique of the previous work has been considerably improved in the interval between 1908 and 1917. The transmitting liquid used in 1908 was a mixture of water and glycerine. and elaborate precautions had to be taken to avoid short circuits. The liquid is now a hydrocarbon, and the insulation properties are perfect. The values now obtained for the change of resistance differ by about 1.5% from the previous ones. Part of this difference is perhaps to be ascribed to improvement in technique, part to change in the behavior of the glass, which has been resting ten years since blowing and annealing, and perhaps part to difference in the standard of pressure. My very earliest results, which reached to only 6500 kg., depended on a pressure gauge of smaller range and somewhat different construction from that used in all my subsequent work reaching to 12000 kg. or more. All this later work depends on the same gauge, and assumes as the fundamental constant that the freezing pressure of mercury at 0° is 7640 kg. Any discrepancy now found with the former values for the resistance of mercury cannot affect the validity of any of the later work up to a range of 12000 kg.

The glass was seasoned before the measurements by an application of 11300 kg. at room temperature, and then by raising temperature to 96° while still under pressure. Five runs were made on the liquid, in addition to the seasoning runs; these were at 0°, 26°, 50°, 76°, and 97°. The maximum zero displacement after a run at any of the temperatures was 0.46% of the total effect. The maximum departure from a smooth curve of any of the observed points at any temperature was 0.6% of the total effect, and the points usually lay on a smooth curve within the sensitiveness of the readings, which was about one part in 5000

of the maximum effect.

The observed results were smoothed for pressure and temperature and a table constructed for the resistance at uniform intervals of pressure and temperature in the regular way. The resistance of the liquid is shown in Table IX, and the coefficients are shown later in Table XX. The resistances given in this table are corrected for the compressibility and thermal expansion of the glass, using the values already given. The correction for temperature amounts to a change of observed resistance of 0.0007 for the range of 100°, which is about 0.74% of the measured effect, and the correction on the pressure effect is 0.0007 for 1000 kg., which is initially 2.2% of the pressure change. The values given in the Table are, therefore, relative values of the

TABLE IX.

RELATIVE SPECIFIC RESISTANCE OF LIQUID MERCURY.

Pressure	Resistance						
kg/cm ²	00	25°	50°	75°	100°		
0	1.0000	1.0240	1.0480	1.0719	1.0959		
1000	.9689	.9911	1.0137	1.0360	1.0574		
2000	.9400	.9609	.9823	1.0032	1.0224		
3000	.9136	.9331	.9533	.9726	.9902		
4000	.8894	.9076	.9268	.9449	.9611		
5000	.8667	.8838	.9023	.9192	.9345		
6000	.8459	.8615	.8793	.8951	9096		
7000	.8263	.8408	.8579	.8729	.8866		
8000		.8214	.8377	.8516	.8650		
9000		.8034	.8200	.8318	.8445		
10000		.7863	.8010	.8133	.8254		
11000		.7704	.7844	.7958	.8071		
12000		.7554	.7684	.7790	.7895		

specific resistance, that is, they are the relative values of the resistance which would be shown by a body of mercury of invariable dimensions, but with the total mass changing with pressure and temperature.

Certain differences between the new and the old results should be mentioned. At 25° the change of resistance under 6500 kg. is now found to be 0.1586, against the old value 0.1562. The previous formula given for the resistance up to 6500 kg. gives rather good results when used for extrapolation to 12000 kg. At 25° the observed decrement of resistance is now found to be 0.2622 against the value 0.2600 computed by the formula previously given. The difference is approximately the same as that between the previous and the present observed values at 6500 kg. Over the narrower temperature range of the previous work the effect of temperature was taken as linear at any constant pressure. Over the greater temperature range of the present work, this is found not to hold, but the effect of temperature becomes greater at the higher temperatures, and passes through a minimum near 25°. At atmospheric pressure, however, the relation between resistance and temperature is still found to be linear within the limits of error, which are about 5/10,000 of the total resistance.

The resistance of the solid under pressure was measured by filling

a capillary of very thin glass with the liquid, exposing to a pressure sufficient to freeze it, and making measurements on the solid contained in the glass without allowing the pressure to fall low enough to melt the mercury. By the use of thin glass I hoped to eliminate error due to the constraining action of the container. It was necessary to use a capillary of rather large section, because of the mechanical difficulties of blowing and handling a very fine capillary with excessively thin walls, and the potentiometer method of measurement was therefore used. The leads were of fine platinum sealed through the glass. Under pressure the glass cracked around the seals, but of course this introduced no error in the measurements of the solid. Only one set of measurements was made on the resistance of the solid, at 0°. Measurements were made on the liquid up to the freezing pressure, pressure was then increased very cautiously beyond the freezing point so that freezing took place slowly, and the solid so formed was seasoned by an excursion to 12000 kg. and back nearly to the freezing pressure. Readings were now made in the domain of the solid to 12000 kg. These readings were exceedingly regular; they showed no departure from the smooth curve within the sensitiveness of measurement, which amounted to one part in 1500 on the total effect for the range 7640 to 12000 kg. This was gratifying, because it showed that the very thin glass exerted no perceptible constraining effect. In the previous work with the liquid in heavy glass capillaries very irregular results were found after the metal had frozen.

The relative values for the resistance of the solid are shown in Table X in terms of the resistance of the solid at 7640 kg. and 0° as unity. In comparing these values with those of the liquid it must be remembered that the values for the solid are relative values of the "observed" resistance, and must be corrected by a factor equal to the linear compressibility in order to give relative values of specific resist-The pressure coefficient of "observed" resistance may be found from the table to be -0.04236, and within the sensitiveness of the measurements it is constant over the pressure range from 7640 to 12000. This value for the pressure coefficient is somewhat higher than the minimum value set in the previous work, which was -0.0_52 . The accuracy of the previous work for the solid was so low that it was stated that the maximum value for the solid might not impossibly be ten times the minimum. The pressure coefficient of the solid is very nearly that of the liquid, which is -0.05224 at 6500 kg., when corrected by one third the volume compressibility of the liquid mercury so as to be strictly comparable with the value for the solid. It is surprising

TABLE X. Relative Specific Resistances of Solid Mercury at 0° C.

Pressure kg/cm ²	Resistance	
7640	1.00000	
8000	0.99185	
9000	0.96870	
10000	0.94615	
11000	0.92405	
12000	0.90250	

The ratio of the resistance of the liquid to that of the solid at the freezing point at 0° and 7640 kg. is 3.345.

that the values for the solid and the liquid are so close, and still more surprising that the value for the solid is greater than that for the liquid. The former rough work suggested the opposite and more natural behavior.

The ratio of the resistance of the solid to that of the liquid at the freezing pressure may also be calculated from the measurements. In view of the extreme care taken to compel the freezing to go slowly, and the fact that when the apparatus was taken apart the capillary was found cracked only at the bend, it is probable that the observed ratio of resistance of solid to liquid refers to the relative resistances of material occupying space of the same dimensions in the liquid and solid states, that is, to relative values of the specific resistance. The value found for the ratio of resistance of liquid to solid at 0° and 7640 kg. (the equilibrium coördinates) was 3.345. This falls within the range of the very irregular values found in the previous work.

Gallium. The raw material from which this rare metal was prepared I owe to the kindness of Dr. K. Stock of the Bartlesville Zinc Co. The purification I owe to the kindness of Professor T. W. Richards. He was engaged in a redetermination of the atomic weight and certain other physical properties, and was kind enough to include some of my raw material with his, and let me have some of the purified product.

The actual work of purification was done by Mr. S. Boyer, under the direction of Professor Richards. The final product had less than 0.01% total impurity. Professor F. A. Saunders was kind enough to make a spectroscopic analysis for me, and was able to detect traces of zinc as the impurity. There may also have been some indium present.

There was available for my measurements about one gram. This was ample for a determination of the effect of pressure on resistance, and also for a determination of the variation of freezing temperature with pressure and an exploration for other allotropic modifications (which had not been previously done) but was not sufficient for a determination of the change of volume on freezing. The complete

freezing data are, therefore, not yet determined.

The measurements here described include the specific resistance of the liquid, temperature coefficient of resistance of solid and liquid at atmospheric pressure, change of resistance when the solid melts to the liquid, effect of pressure on resistance of both solid and liquid,

and variation of freezing pressure with temperature.

The determination of the freezing curve and the exploration for new modifications was the first task, in order to fix the range over which the resistance measurements were to be extended. Gallium is, of course, abnormal in that it expands when it freezes, and the freezing temperature is accordingly depressed under increased pressure. It would not be unnatural to expect new modifications at high pressures like the other modifications of ice. Because of the limited quantity of material available the method of exploration for new modifications had to be an electrical one. It was my original intention to form the material into wire by extrusion, and to measure the resistance of the solid as a function of pressure at different temperatures. A change from one modification to another would be shown by a discontinuous change of resistance, and melting by open circuiting. Unexpected difficulties were found in the extrusion. If the extrusion is performed at room temperature, the metal melts under the one-sided stress instead of extruding (the melting temperature is 29.85°), and if this effect is avoided by lowering the temperature. the metal becomes so exceedingly stiff and brittle that extrusion is very difficult. After an unsuccessful attempt at room temperature, I tried extrusion at the temperature of ice and salt. At this temperature the metal spit out of the die in short pieces. However, by careful work, I did get a few inches of wire at this extrusion temperature. Perhaps some intermediate temperature would be more successful. Mechanically the extruded wire is very crystalline and brittle, and will support almost no bending. When enclosed in a glass capillary, however, and if the capillary breaks across without breaking the gallium, as sometimes happens when the capillary is ruptured by freezing, the metal may be pulled out by a tensile stress and appears as ductile as lead.

The extruded wire was used in an attempt to find the melting curve. Short lengths were layed horizontally between two copper wires, short-circuiting them. It was expected that when melting took place the system would open circuit. The surface tension of the gallium proved to be so high, however, that this method did not work. The metal, even when melted, only sagged between the supports, and no measurements could be made. Several modifications of this scheme were tried with indifferent success. These preliminary measurements made pretty evident, however, that there were no new modifications, and that above the normal melting point the metal remains liquid at all pressures below 12000 kg.

Measurements were now made on the resistance of the liquid as a function of pressure above the melting temperature. The liquid gallium was enclosed in a glass capillary, provided with four platinum terminals, and measurements made by the potentiometer method. The capillary was filled in high vacuum to avoid error from air sticking to the walls. From a comparison of the resistance of the capillary when filled with gallium and when filled with mercury it was possible to obtain the resistance of gallium in terms of that of mercury, and so

the specific resistance of liquid gallium.

After completion of measurements on the liquid, the temperature of the apparatus was lowered into the region of the solid, and after some trouble, the liquid was induced to freeze. The melting curve was now determined by finding, as a function of temperature, the pressure at which the resistance began to change discontinuously. It was necessary to do this very cautiously. In changing pressure the thermal effects of compression might easily be sufficient to entirely melt the gallium, when long and tedious manipulation would be necessary to make it freeze again, because of the well known property of supporting great subcooling. In this way the melting curve was mapped out to 12000 kg.

Measurements were also made on the resistance of the solid as a function of pressure while enclosed in the glass envelope, but there were irregularities, and it was evident that the solid must be unconstrained in order to give reliable results. Accordingly a small rod

of solid gallium was sculptured out with considerable difficulty with a warm wire as a sculptor's tool, four platinum terminals were set into it, and measurements made of the pressure coefficient of resistance by the potentiometer method. The temperature coefficient of the solid at atmospheric pressure was also determined with this free specimen. This seems to be the first time that this has been done. Previous measurements of the temperature coefficient of the solid have been on the solid in glass, and no correction has been applied for the constraining effect of the glass. After the completion of the resistance measurements on the free solid another point was found on the melting curve, which checked with the points found previously. The resistance of the solid showed no discontinuities within the errors of the measurements, and hence it is not likely that there are new modifications in the region of the measurements. This was rather a disappointment.

TABLE XI.
GALLIUM.
Melting Curve.

Pressure kg/cm°	Temperature °C.
0	29.85°
1000	27.8
2000	25.7
3000	23.55
4000	21.4
5000	19.2
6000	17.0
7000	14.8
8000	12.6
9000	10.35
10000	8.10
11000	5.85
12000	3.55

The smoothed coördinates of the melting curve are given in Table XI, and the observed points with the curve are shown in Figure 8. For the melting point at atmospheric pressure I used the value determined for this sample by Mr. Boyer, which is 29.85°. This is lower than the value originally given by deBoisbaudran, 14 30.15°,

but is higher than that given by Guntz and Broniewski, ¹⁵ 29°. The value of Boyer is the mean of a number of values determined with extreme care, and is seen to fit perfectly with the values which I have found at higher pressures. Considering the extreme purity of this sample, there is every reason to give this value the preference.

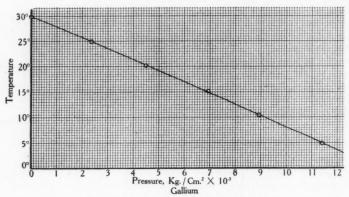


FIGURE 8. The melting curve of gallium.

The melting curve has the same form as that of water and bismuth, the only other substances I know with curves of this abnormal type. It is characteristic of these curves that the slope becomes numerically greater at the higher pressures. The slope of the melting curve of gallium increases numerically by about 15% in the pressure range of 12000 kg.

The slope of the melting curve may be combined with other data to give the latent heat on melting. Boyer's values for the densities of the solid and liquid at the melting point are 5.90 and 6.09 respectively. This gives 0.00529 for the change of volume per gm. on melting. Taking from the above curve the value 0.00203 for the initial slope of the melting curve, and substituting in Clapeyron's equation, we find 18.5 cal. per gm. as the latent heat of melting. Boyer has recently determined this to be 19.1. The agreement is probably within the error of the density determinations. The variation of the latent heat along the melting curve cannot be found until the variation of the change of volume along the melting curve is also known, and this will require a larger sample.

The ratio of the resistance of the liquid to that of an equal volume

of mercury at the melting point was found to be 0.2683, against the value, 0.272 of Guntz and Broniewski. Taking for the specific resistance of mercury at this temperature 96.59×10^{-6} , this gives 25.92×10^{-6} for the specific resistance of liquid gallium at the melting point.

Three runs were made on the resistance of the liquid as a function of pressure, at 34.2° , 62.5° , and 94.4° . Before the final measurements another run was made on another sample. This run had somewhat greater error, but agreed with the final results within the irregularities of the measurements. The resistance measurements of the liquid showed a distinct hysteresis, doubtless due to the action of the glass capillary. Any such effects would be expected to be especially large for gallium because the pressure coefficient of resistance is so low. The difference between readings with increasing and decreasing pressure might amount to 2.5% of the maximum effect. Except for this, the points lay regularly within the sensitiveness of the readings. The values obtained from these three runs were smoothed in the regular way, and the resistance tabulated at regular intervals of temperature and pressure. The results are shown in Table XII. In this table

$\frac{\rm Pressure}{\rm kg/cm^2}$	Resistance 65° 10			
0	0.6456	0.6647	0.6824	
1000	.6415	.6605	.6783	
2000	. 6380	.6564	.6743	
3000	. 6342	.6527	.6705	
4000	.6308	.6488	.6667	
5000	.6272	.6452	. 6629	
6000	.6238	.6418	. 6593	
7000	. 6205	.6383	.6558	
8000	.6171	. 6349	.6522	
9000	.6139	.6316	.6486	
10000	.6105	.6283	.6451	
11000	.6075	.6252	.6418	
12000	.6044	.6223	. 6386	
Average	-			
Coefficient 0-12000	-0.0 ₅ 531	-0.0 ₅ 532	-0.0534	

the unit of resistance is the resistance of the solid at atmospheric pressure and 0° C. There may be some question as to the accuracy of the value for the ratio of resistance of solid to liquid, but this cannot affect the relative accuracy of the values listed in the table for the resistance of the liquid.

The values listed in the table have been corrected for the thermal expansion and compressibility of the glass, so that the values are proportional to the specific resistances. In making this correction the thermal expansion of the glass was assumed to be 0.058, and the linear compressibility 0.067. The correction for thermal expansion is small, and any error in the value assumed for the coefficient cannot appreciably affect the results, but because of the smallness of the pressure coefficient of resistance, the correction for the compressibility of the glass is rather important. The correction for compressibility, as given in the table, amounts initially to 11% of the pressure coefficient. The compressibility of different varieties of glass varies a good deal; it is perhaps conceivable that the value assumed is as much as 20% different from the correct one, so that the possibility must be recognized that the values given in the table for the pressure coefficient of resistance may be in error by as much as 2%. However, any correction of this sort will not affect the relative curvature, since the compressibility of glass is sensibly linear, and it seems justified to retain all the significant figures of the table. The effect of the corrections for the glass is to increase both the observed temperature and pressure

The average pressure coefficient of the liquid to 12000 kg. is seen to vary little with temperature. In absolute value it is somewhat less than one half that for bismuth, and one sixth that for liquid mercury. The curvature is in the normal direction, that is, the coefficient becomes less at the higher pressures.

coefficients of resistance.

The pressure coefficient of resistance of the solid was measured only at 0° ; at this temperature the entire pressure range of 12000 kg. was available, whereas at higher temperatures the pressure range was restricted by the melting, and the accuracy was proportionally less. The absolute resistance of the specimen was low, so that measurements could not be made with as much accuracy as usual. Beside the final run from which the tabulated results were taken, several rougher runs were made with other samples; these agreed with the final results within the accuracy of the measurements. Within the limits of error the relation between resistance and pressure is linear at 0° to 12000 kg., and the coefficient is -0.0_5247 . The maximum departure of

any of the observed points from a linear relation was 2.7% of the total effect.

The constraining effect of a glass capillary on the solid is shown by the low value, -0.0_5191 , found for the coefficient of the solid in glass.

The pressure coefficient of the solid is seen to be negative, that is, normal. This was rather a surprise; I had anticipated because of the abnormal expansion on freezing and the fact that bismuth also expands on freezing and has a positive coefficient of resistance that the coefficient of gallium might be positive also. The numerical value of the coefficient of the solid is quite normal, when compared with other metals. It is the value characteristic of a hard metal, which in most other cases also means a metal with a high melting point. The coefficient of the solid is of the order of one half that of the liquid. This again is as one would expect, except for the abnormal volume relations on freezing. However, the solid is less compressible than the liquid in spite of its greater volume ^{15a}; so that from this point of view the relative magnitudes of the pressure coefficients of liquid and solid do not seem unnatural.

The temperature coefficient of resistance of the unconstrained solid was obtained from readings at 0° and 21.5°. The value for this range is 0.003963, an entirely normal value. Previous values for this coefficient are exceedingly uncertain. Guntz and Broniewski's readings were quite irregular, the effect even reversing in sign above 18.6°. This may have been due to the constraining effect of the glass; such an effect is to be expected, and in the observed direction.

It may be mentioned that I made measurements on the subcooled liquid at 0°, and found the resistance to lie on a regular prolongation of the curve for the resistance above the melting point. Guntz and Broniewski, on the other hand, found the resistance of the liquid to pass through a minimum and to increase again in the unstable region

below the melting point.

The ratio of the resistance of the solid to that of the liquid at the freezing point was found from measurements of the resistance of the solid at 0° in the glass capillary and the resistance of the liquid in the same capillary. The resistance of the solid was extrapolated to the melting point with the coefficient found. This procedure may be open to some question, but it seemed as satisfactory as any other that presented itself. The specific resistance of the solid was found to be 1.733 times that of the liquid at the melting point. Notice that the relative magnitude of the volumes governs the relative magnitudes of the resistance; the solid with the larger volume also having the larger

resistance. Guntz and Broniewski found 2.09 for the ratio of the two resistances.

TITANIUM. By the kindness of the Research Laboratory of the General Electric Co. I was enabled to make measurements on a filament of titanium deposited on tungsten, which had been used for experimental work with incandescent lamps. The dimensions of the tungsten core were such that the total impurity of tungsten was only 1.8%. The method of deposition of the titanium on the core is not known to me; the surface of the filament was distinctly crystalline in appearance, probably due to recrystallization after deposition. It had been glowed out in vacuum at high temperature after deposition in order to remove impurities of hydrides, nitrides, and oxides, all of which are readily formed with this substance. This glowing out must have produced alloying with the tungsten core, and the alloy so formed is evidently quite different in its properties from the pure metal. This may be stated with confidence because the General Electric Co. found for the specific resistance of this filament the value 350×10^{-6} ohms per cm. cube, which is higher than would be given by the tungsten core alone. The same thing is indicated by the low value of the temperature coefficient, which was 0.000221.

The difficulties of the pressure measurements were very great, and it was not possible to obtain results which were at all regular. It can be stated only that the pressure coefficient is exceedingly small, probably not greater than 10⁻⁷ per kg., and that the likelihood is that

the resistance increases with pressure.

ZIRCONIUM. Two filaments deposited on tungsten in the same way as the titanium were made available through the kindness of the General Electric Co. The treatment of the filaments had been the same as that of titanium. It is probable that the temperature of glowing out had been sufficient to produce alloying with the tungsten core. This is strongly suggested by the low value for the temperature coefficient of resistance, which, between 0° and 100°, was 0.00004 for one specimen, and 0.00058 for the other. The dimensions of the wires on which these filaments were deposited would indicate a total impurity of tungsten of 1.8% and 0.6% for the two samples respectively. The impurer sample has the smaller coefficient, as is usual. The exceedingly low value of both coefficients indicates that the impurity has a specific effect, and that any results found for the pressure coefficient may not be very close to the values for the pure metal.

In view of the probably large effect of the impurity, and also of the difficulty of the measurements, a great deal of effort was not put on this substance. The potentiometer method of measurement was used. This substance cannot be soldered, so that it was necessary to make connections with fine springs; slipping of the springs was perhaps accountable for some of the irregularities. The surface layer has a very high resistance, which again introduced irregularities at the spring contacts.

Two runs were made on the impurer specimen, at 0° and 94°. The irregularities of the second run were so great that the results were not computed. Within the limits of error the relation between pressure

and resistance is linear at 0° , and the coefficient is -0.0_65 .

The results on the second and purer sample were much more regular. Readings were made at 0° and 95° . At both these temperatures the relation is linear to 12000 kg. The best value for the pressure coefficient is $-0.0_{\rm e}398$ at 0° , and $-0.0_{\rm e}396$ at 95° . The coefficient is seen to be very small; such small values have been found only for certain of the high resistance alloys. The specific resistance of these Zirconium filaments was also very high; 200×10^{-6} ohms/cm³ is the value given me by the General Electric Co.

Arsenic. Considerable interest attaches to this element because of its position in the periodic table above bismuth and antimony and below black phosphorus, all of which are abnormal in behavior under pressure. The arsenic used in this experiment was furnished by Eimer and Amend. It had been distilled in vacuum, but was otherwise of ordinary commercial quality, and I have no way of knowing what the impurities might have been. I attempted to cast it in a mold of pyrex glass, supported on the outside with magnesia, and enclosed in an iron pipe with caps tightly screwed on the ends. The melting temperature of arsenic was high enough to melt the pyrex, however, and the arsenic was found after the heating in the form of a solid slug in the lower part of the magnesia powder. It may possibly have come in contact to a slight extent with the iron of the pipe while in the molten condition. A slender rod about 1 mm. square in section and 2 cm. long was worked out of the slug with a file and a hack saw and by grinding. Grooves were filed on the ends, connections made with spring clips, and measurements made with the potentiometer in the regular way. I was surprised to find after I had completed the measurements that Matthiesen 16 had soldered connections to arsenic, and I verified for myself that it is as easy to soft solder to this metal as to antimony, for example. In fact the completely metallic character of the massive casting is a surprise contrasted with the appearance of the sublimed material as ordinarily furnished. Of

course if I ever repeat this work I shall make connections by soldering.

A measurement of the temperature coefficient of resistance showed a discouragingly high probable impurity; the average coefficient between 0° and 95° was 0.00076, whereas Matthiesen 15 had found 0.0038. The high probable impurity of this sample did not make it worth while to make any very extended pressure measurements. One run was made. There were considerable irregularities, but within the limits of error the relation between pressure and resistance is linear to 12000 kg., and the value of the coefficient is $-0.0_{\circ}326$.

This coefficient is similar to that of a number of metals both as regards magnitude and sign. Arsenic is seen therefore to acquire neither the abnormal sign of the coefficient of its neighbors bismuth and antimony on the one side, nor the abnormally high numerical

value of the coefficient of black phosphorus on the other.

LIQUID BISMUTH. The pressure coefficient of resistance of solid bismuth is abnormal in being positive; it was of particular interest to find whether the same abnormal behavior holds for the liquid. The bismuth used for these measurements was from the same lot of electrolytic bismuth as that whose pressure coefficient was previously measured. It was melted into a U-shaped fine glass capillary provided with four sealed-in platinum terminals for use with the potentiometer method. Special precautions were necessary to prevent the bismuth from cracking the capillary on freezing; this was accomplished by very slow cooling from the bottom up after the capillary had been filled with liquid bismuth. In this way congealing ran upward from the bottom of the capillary toward the open top, and no liquid was entrapped by the solid to crack the glass by its expansion on freezing.

A special arrangement of the pressure apparatus was necessary to permit the electrical measurements. The same arrangement was also used with lithium, sodium, and potassium, but since the apparatus was first used with bismuth, it will be described here. The difficulty was with the insulating plug, which was packed with soft rubber. This would have been carbonized by the temperature of melting bismuth. The pressure apparatus was accordingly constructed in three parts, instead of the customary two. There was an upper cylinder, as usual, in which pressure was produced, and in which was located the measuring coil of manganin wire. This upper cylinder was connected by a stout tube with the cylinder below it, in which was placed the bismuth in the glass capillary. This second cylinder was surrounded with a bath of Crisco, by which the desired temperature was maintained by thermostatic regulation. Out of the bottom of the

second pressure cylinder was led another piece of stout tubing, which passed through a stuffing box in the bottom of the Crisco bath, and below the bath connected with a third pressure cylinder. This third cylinder was kept cool by a bath of water at room temperature. This bath was stirred to maintain the temperature uniform, but it was not necessary to regulate the temperature thermostatically. In the lower pressure cylinder was situated the insulating plug, of the same design as used in all the work with the potentiometer method. The plug was connected with the bismuth in the second cylinder by four insulated leads brought down through the pipe connecting the second and third cylinders. The insulation of these wires was asbestos; asbestos covered copper wire is now a commercial product. In this way the insulating plug was kept cool, so that there was no danger of leakage or failure of insulation because of the high temperature. The only trouble to be anticipated was large parasitic e.m.f.'s because of the large differences of temperature, but the parts in which there were temperature gradients were composed of electrically homogeneous material, and no more trouble was found from this effect than at

ordinary temperatures.

Runs were made on liquid bismuth at 274.6°, 260.0°, and 239.6°, in this order. For fear of damaging the capillary (fused in platinum leads almost always make trouble under pressure) the pressure was not raised to the maximum of this work, 12000 kg., until the last run, so that I did not obtain data for the resistance of the liquid over the entire possible range. At 239.6°, however, pressure was run to the maximum with no bad effects. After the measurements on the liquid, the bismuth was allowed to freeze under pressure, and measurements were attempted on the solid. The results for the solid were not good, however, probably because of strains introduced on freezing in the fine capillary. There was no way of controlling the freezing under pressure and making it take place from the bottom up as had been possible in initially setting up the apparatus. The effects of strains were apparent in two ways; the pressure coefficient of resistance of the solid was negative over part of the range below the solidifying point, whereas that of the unconstrained solid is positive, and the freezing point was depressed a couple of degrees, which is in the direction to be expected if there are internal strains. Irregularities introduced by these strains are of importance, however, only when it was desired to obtain the relative changes of resistance with changes of pressure, and it was possible to find a value for the change of resistance on solidifaction which should not be greatly in error.

The readings on the liquid went very smoothly. Within the limits of sensitiveness there was no difference between points obtained with ascending or descending pressure, and except for one point, all of the observed points lay on smooth curves within the sensitiveness of reading, which was about 0.2% of the total effect. The observed values, smoothed for temperature and pressure, are shown in Table XIII in terms of the resistance at the melting point at atmospheric pressure as unity. The values tabulated are "observed" values, that is, they have not been corrected for the thermal expansion or

TABLE XIII.
BISMUTH.

Relative Values of Observed Resistance of the Liquid in Glass Capillary.

Pressure kg/cm ²	275°	Resistance 260°	240°
- 0,			
0	1.0019		
1000	.9900		
2000	.9789		
3000	.9684	.9617	
4000	.9584	.9520	
5000	.9490	.9426	
6000	.9400	.9336	.9253
7000	.9314	.9249	.9169
8000		.9167	.9088
9000			.9008
10000			.8931
11000			.8855
12000			.8783

The resistance of the liquid at atmospheric pressure and 271.0° is taken as unity.

compressibility of the glass capillary. It did not seem best to do this because of the uncertainty in the values for the glass at the temperatures and pressures of the measurements. The glass used for the capillary was an ordinary soft soda glass. The best value for the cubic compressibility is probably 2.7×10^{-6} , taking Amagat's values for the compressibility and temperature coefficient of compressibility, and for the linear thermal expansion the best value is probably 8×10^{-6} .

The most important result shown by the table is that the pressure coefficient of resistance of the liquid is negative like all normal metals.

The positive coefficient of the solid is therefore presumably due to its crystalline structure. The liquid behaves in other ways also like normal metals. When resistance is plotted against pressure, the curve is convex toward the pressure axis; that is, the pressure coefficient decreases relatively (and also absolutely) at the higher pressures. The pressure coefficient is little affected by temperature, within this range, and also the temperature coefficient is little affected by pressure. The initial pressure coefficient of the "observed" resistance at 275° is -0.04123, which corrects, using the constants above, to -0.04132 for the specific resistance. Both of these coefficients are to be distinguished from the pressure coefficient of the "observed" resistance of a solid. The pressure coefficient of the liquid is of the same magnitude as that shown by the softer solid metals, such as lead, and is also very nearly the same numerically, although of opposite sign, as that of solid bismuth.

The temperature coefficient of the "observed" resistance at 275° is 0.00047, which corrects to 0.00048 for the coefficient of the specific resistance. This is about five times less than the value for a normal solid at the same temperature. It is almost always true that the temperature coefficient of the liquid is materially less than that of the solid.

At 7000 kg. at the equilibrium point, the resistance of the liquid is approximately 45% of that of the solid. At atmospheric pressure Northrup and Sherwood ¹⁷ found for the ratio 43%. There was considerable preliminary rounding of their melting curve, so their results are probably not any more accurate than mine, but it is at any rate evident that this ratio does not suffer any large change with increasing pressure.

Tungsten. In the preceding paper ¹⁸ results were given for the pressure coefficient of resistance of tungsten, but the value of the temperature coefficient of resistance of the sample used was so low (0.00322) that it was probable that the tungsten was not very pure. Since the publication of my earlier paper Beckman ¹⁹ has measured the effect of pressure to 1600 kg. on the resistance of a sample of tungsten having a considerably higher temperature coefficient than my original piece, and has found a higher initial value of the pressure coefficient than I did.

The sample of tungsten on which I previously experimented was the purest which the General Electric Co. was at that time in a position to offer me. I have since learned that it was probably "doped," that is, thoriated, the impurity of thorium being 0.2 or 0.3%. Through

the kindness of the manufacturers I have since been able to measure the resistance of two samples of "undoped" tungsten of high purity. The Westinghouse Lamp Works gave me a specimen which they estimated to contain less than 0.03% total impurity, and the Research Laboratory of the General Electric Co. placed at my disposal a specimen which they estimated to be even purer. Judging by the test of the temperature coefficient the General Electric sample was appreciably purer. The average temperature coefficient between 0° and 100° of the Westinghouse sample was 0.003925, and that of the General Electric sample 0.004209.

Pressure measurements were made on both samples, but only those on the purer are given in detail here. The treatment of both specimens was the same. The wire was 0.002 inches in diameter; it was wound bare on a bone core, and connections were made by fusing to it pure nickel wire with an arc in hydrogen. This method of making

TABLE XIV.
TUNGSTEN.

Temp.	Resistance	P	ressure Coeffic	Maximum Deviation from	Pressure of Maximum	
		At 0 kg.	At 12000 kg.	0-12000	Linearity	Deviation
0	1.0000	-0.05143	-0.05131	-0.0 ₀ 1346	.00015	5500
50	1.2084	137	133	1340	7	7000
100	1.4209	140	136	1368	14	7500

connections was taught me by the General Electric Co., and is simpler than the combination of gold and platinum which I formerly used, although the former connection was just as satisfactory electrically. The wires were seasoned by a long preliminary heating to 125° and by an application of 12000 kg. Three runs were made, at 0°, 50°, and 95°. Except for two bad points, the greatest departure of any of the observed points from a smooth curve at any of the three temperatures was 0.2% of the total effect, and the displacement of the zero after a run was not greater than the irregularity of the other points. The observed results were smoothed, and a table constructed for the resistance as a function of pressure and temperature by regular methods. The results are shown in Table XIV and Figure 9. The

relation between pressure and resistance is nearly linear, and the departure is in the normal direction, that is, the coefficient becomes less at the higher pressures. The results are somewhat unusual in that the pressure coefficient does not advance regularly with increasing temperature, but is less at 50° than at either 0° or 100°. The same behavior was shown by the impurer sample also, and is doubtless real. The departure from linearity is also less at 50° than at either 0° or 100°.

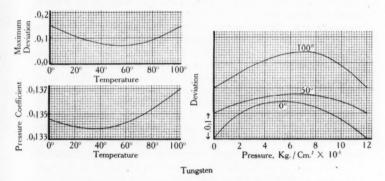


Figure 9. Results for the measured resistance of tungsten. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

The results for the impurer sample were similar, but the numerical values were different. The average coefficients to 12000 at 0° , 50° , and 100° being respectively $-0.0_{5}1387$, 1331, and 1362. These may be compared with the values of the Table; the differences are of the order of 0.5% at 50° and 100° , but the difference rises to 3% at 0° . At 0° the coefficient of the impurer is larger, and at the two other temperatures is smaller.

These results may be compared with those recently published by Beckman. ¹⁸ He finds for the average temperature coefficient of his sample 0.00399, which is a trifle higher than that of the impurer sample above. His initial pressure coefficient at 0° is -0.0_5151 , reduced from atmospheres as the pressure unit to kg/cm². This value is 2.7% higher than that of the impurer of the two samples above, and 5.6% higher than that of the purer. A comparison of the present results with my former ones shows that both of my new samples,

which are purer than my former one, have a higher pressure coefficient. It is evident that the sign of the effect of impurity on the pressure coefficient cannot be predicted with probability, as can the effect of impurity on the temperature coefficient. At the same time the fact is to be emphasized, previously already found to hold in a number of cases, that the effect of impurity on the pressure coefficient is usually much less than on the temperature coefficient. Thus in the present case, a change in the temperature coefficient of 31% (present compared with former work) is accompanied by a change of pressure coefficient of only 9%.

LANTHANUM. This material I owe to the kindness of Professor Charles Baskerville, who had prepared it from the fused salts by electrolysis. No chemical analysis was available, but a spectroscopic analysis by Professor F. A. Saunders showed a large amount of Mg (possibly 10-20%) and a considerable amount of Si. There was a trace of Ca, no Ba, and none of the other rare earth metals were detected. The rare earths tested for were Ce, Pr, Nd, Er, Y, Yt, Dv, A nodule about one gram in amount was available for the measurements. A small homogeneous piece was cut from the nodule, and extruded to wire in a small die of special construction. It is necessary to heat to about 450° to extrude, and even then the extrusion is a matter of some difficulty. The wire so formed is exceedingly stiff; it is evident that its elastic constants and its elastic limit are both high. It is quite brittle, and can be bent only into a circle of large radius. I prepared two pieces of wire, one at a somewhat higher extrusion temperature than the other; the mechanical properties seemed unaffected by the temperature of extrusion. The wire on which measurements were made was only 1.7 cm. long, and was that prepared at the lower extrusion temperature. In order to attach the four terminals, spring clamps of special design had to be used; it is not possible to solder this metal. The clamps gave some difficulty with shifting of position, and the results were not so regular as usual.

The temperature coefficient of this material between 0° and 100° was only 0.001476. This is very low, and indicates that the material was not very pure. For this reason it did not seem worth while to spend a great deal of effort on the pressure measurements, although these could have been improved by repeating the measurements with a longer specimen, which was obtained after the easiest extrusion temperature was discovered.

Two runs were made for the pressure coefficient, at 0° and 50° . The ascending points of the run at 0° were entirely regular, but the

descending points were irregular, probably because of slipping of the contacts. At 50° the ascending and descending points agreed more closely, but there were irregularities both ascending and descending, less in magnitude than at 0° , and averaging 2.7% of the maximum pressure effect.

The results are collected in Table XV and Figure 10; they are seen to be quite normal. The pressure coefficient is negative, and

TABLE XV. LANTHANUM.

Temp.	Resistance	P	ressure Coeffici	ent Average	Maximum Deviation from	Pressure of Maximum
		At 0 kg.	At 12000 kg.	0-12000	Linearity	Deviation
0	1.0000	-0.0539	-0.0525	-0.0 ₅ 331	.0020	5800
50.	1.0752	39	36	377	°4	5800
100	1.1476					

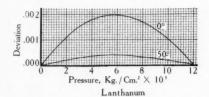


Figure 10. The deviations from linearity of the measured resistance of lanthanum in fractional parts of the resistance at 0 kg, and 0° C.

increases at the higher temperatures. The relation between pressure and resistance is also normal, the coefficient being smaller at the higher pressures. It is perhaps unusual that the departure from linearity is less at the higher temperatures. The deviations from linearity are so small and so nearly symmetrical about the mean pressure that it is not necessary to reproduce the deviation curve graphically.

I have been able to find no previous values for the specific resistance of this metal. The approximate value for the specimen above,

obtained from micrometer measurements of its dimensions, was 59 \times 10⁻⁶ ohms per cm. cube.

Neodymium. This, as well as the lanthanum, I owe to the kindness of Professor Baskerville. Professor Saunders was kind enough to make a spectroscopic analysis of this also. He found a large amount of Mg, a little Si and La, a trace of Ca, no Ba, and nothing else recognizable. He tested for the rare earths Ce, Pr, Y, Yt, Lu, Dy, Er. The form and method of preparation of the specimen was essentially the same as that of lanthanum. It was extruded into wire 0.020 inches in diameter at 450°. The extrusion was materially easier than that of lanthanum. The wire is not so stiff, and may be straightened after extrusion without fear of breaking. Nevertheless it obviously belongs to the metals with high elastic constants and high elastic limit. The specimen used for the measurements was 7.1 cm. in length; the manner of attachment of the connections was the same as with lanthanum. The greater length of the specimen, and perhaps greater skill in handling it, led to much more regular results.

A preliminary measurement of the temperature coefficient was made at 0°, 50°, and 95°. Within this range the relation between temperature and resistance was found to be linear, and the coefficient was 0.000799. This is extraordinarily low, much lower than for lanthanum even, and it did not seem worth while to expend a great deal of time on the pressure measurements.

Two runs were made for the pressure coefficient, at 0° and 50°. The results were rather regular. There was no difference between readings with increasing and decreasing pressure, and the zero was well recovered. The maximum departure of any single point from a smooth curve was 2.6% of the total effect at both 0° and 50°. The numerical results are shown in Table XVI. The values are quite

TABLE XVI.
NEODYMIUM.

Temp.	Resistance	Pr	. Pressure Coefficient Average			Pressure of Maximum
-0.		At 0 kg.	At 12000	0-12000	from Linearity	Deviation
0	1.0000	-0.0 ₅ 238	-0.0₅183	-0.0 ₆ 213	.00078	6000
50	1.0400	250	197	226	87	6000

normal. The coefficient is negative, and becomes greater numerically at the higher temperature. The departure from linearity with pressure is in the normal direction, the coefficient being less at the higher pressures. The departure from linearity is symmetrical, a second degree curve accurately reproducing the results, so that it is not necessary to draw the deviation curves. The deviation becomes greater at the higher temperatures, as is normal.

I can find no tabulated values for the specific resistance of neodymium. The value for the specimen above, obtained from micrometer measurements of its dimensions, was 107×10^{-6} ohms per

cm. cube, about twice the value for lanthanum.

Carbon. These results on carbon must be regarded as of an entirely tentative and orienting character. Present technical methods are not yet sufficiently perfect to permit of the manufacture of carbon, either amorphous or graphitic, of specifiable or reproducible properties. Any massive form of carbon always contains at least a slight amount of binder of unknown properties, amorphous carbon is always impure with a slight amount of graphite, and the purest graphite contains a small and unknown amount of amorphous carbon.

Experiments were made on three samples of carbon. The first of these was supposedly amorphous carbon, an arc carbon made by an unknown German firm. The second was Acheson graphite cut from a piece of graphite furnished by the Acheson Co. for a resistance furnace, and presumably not made with any unusual precautions. The third specimen of graphite was also Acheson graphite, furnished by the Acheson Co., in response to a special request for graphite of the greatest obtainable purity. It was stated by them to contain the minimum of binder, and to have been graphitized with unusual thoroughness, but otherwise its properties were not known.

In view of the unreproducible character of the results it will not

pay to give them in great detail.

Two sets of readings were made on the gas carbon, a complete run to 12000 kg. and back at 30°, and a few readings at 96°. This specimen was about 3.5 inches long, and 0.154 inches diameter. Measurements were made by the potentiometer method, using the three terminal plug as usual. Connections were made to the carbon with spiral springs snapped into grooves filed around the surface of the rod. A preliminary seasoning was made to 6000 kg., but there was very little permanent change of resistance. At 30°, the resistance decreases with rising pressure, and the direction of curvature is normal, that is, the proportional effect becomes smaller at the higher pressures. The

percentage decrease of resistance was 6.68% at 6000 kg., and 12.07% at 12000 kg. At 96°, up to 3000 kg., the coefficient is about 4% greater. The resistance decreases linearly with temperature between 0° and 100°, the total decrease for 100° being 2.56% of the resistance at 0°. The readings on this carbon were entirely regular, showed little difference between ascending and descending values, and an almost

perfect recovery of the zero.

The first specimen of Acheson graphite was cut from a rod of 1.5 inches diameter to about the same dimensions as the gas carbon. Measurements were made by the same method. Three complete series of readings were made, at 0°, 51°, and 97.4°. The readings were not so regular as with the gas carbon, showing large hysteresis effects, rising at the maximum to 12% of the total pressure effect, and there were also parasitic e.m.f.'s so large as to necessitate a special arrangement of the constants of the circuit. The sign of the effect is positive, the reverse of what it is for gas carbon, and there is very considerable departure from linearity with pressure, the coefficient becoming numerically less at the higher pressures. The total fractional increase of resistance under 12000 kg. decreases with rising temperature, being 4.75% at 0°, 4.23% at 50°, and 4.23% also at 100°. The large departure from linearity may be judged from the fact that at 6000 kg. at 0° the increase of resistance is 3.44%, which is 72% of the increase under 12000 kg. The resistance decreases with rising temperature at atmospheric pressure, and the change is not linear. At 0° the resistance on an arbitrary scale is 1.0000, at 50° 0.9135, and at 100° 0.8687.

The second specimen of graphite, supposed to be especially pure, was subjected to a special preliminary seasoning in order to eliminate as far as possible the pores. It was sealed into a lead tube and subjected to a fluid pressure of 12000 kg. on the outside of the tube. The diameter of the specimen was reduced by about 2%, but there were a great many pores still visible to the naked eye. It was further seasoned by heating to 125° in vacuum; this treatment should have removed all moisture, of which no traces, however, were evident. This specimen was cut to the same dimensions, and measurements made in the same way as on the two preceding samples. Only one run was made, at 50°. This was terminated by an explosion at 12000 kg. In view of the unreproducible character of the results it did not seem worth while to repeat the effort to obtain a complete set of readings. As with the other sample of Acheson graphite, the effect of pressure is to increase the resistance, but the change was much less

numerically than for the other piece, and the departure from linearity was much greater, suggesting strongly that at a high enough pressure the resistance may pass through a maximum. The following increases of resistance were found at 2000, 4000, 6000, 8000, and 10000 kg. respectively; namely, 0.69%, 1.25%, 1.62%, 1.79%, and 1.86%. The temperature coefficient of resistance of this specimen was not measured.

Although the results obtained above are not of much accuracy and are not reproducible, two interesting facts stand out; the opposite signs of the pressure coefficient for carbon in the amorphous and graphitic states, and the large departure of the effect from linearity with graphite, indicating a maximum. No substance has yet been found in which a maximum or minimum of resistance has been actually

reached at high pressures.

SILICON. It is well known that technical means are as far from perfect for producing a pure and reproducible silicon as they are for carbon. For instance, the temperature coefficient of resistance varies in sign with different pieces of apparently the same manufacture. In view of this situation it was worth while to make only a few pressure measurements in order to establish the general nature of the effects. Two specimens were used, both provided by the General Electric Co.

The first sample had not been manufactured by them, but had been obtained from the Carborundum Co. It was in the form of a cylinder about 5 mm. in diameter and 8 cm. long. Connections were made with spring clips, and measurements made by the potentiometer method, as usual. The effects were very irregular; I satisfied myself that the irregularities were inherent in the material itself. There were large seasoning effects on the first application of pressure, there were always permanent changes of zero after a run, and there were differences between the readings with increasing and decreasing pressure in a direction the reverse of hysteresis. Two series of runs were made, at 0° and 52°. The resistance decreases under pressure, as is normal. At 0° the total decrease under 12000 kg. was $14.0\%_o$, and at 52° 15.8%. The effect is not linear with pressure, but the coefficient becomes less at the higher pressure, as is normal. The average temperature coefficient of this sample between 0° and 52° was 0.000117.

The second sample was also furnished originally by the Carborundum Co., but it had been partially purified by the General Electric Co. by melting in vacuum. The purification was by no means complete, for it was possible to see with the naked eye small slag-like inclusions

and there were numerous fairly large pores. (There were visible pores in the first sample also). It need not be anticipated that the pores cause any error in the pressure coefficient, for the transmitting liquid freely penetrates the pores and transmits pressure uniformly to all parts; there is never any permanent change of dimensions after an application of pressure. The second sample was of approximately the same dimensions and was treated in the same way as the first. Two sets of readings were made with this second sample, at 0° and 95°. The pressure coefficient is negative in sign, as it was for the first sample, but the numerical values are somewhat different. At 0° the resistance decreases by 10.1% under 12000 kg., and at 95° by 15.3%. The change is not linear with pressure, but the coefficient becomes larger at the higher pressures, which is the opposite of the normal behavior of the first sample. The temperature coefficient of this sample between 0° and 95° was + 0.0000615, about half as large as that of the first sample.

In spite of the very marked differences these two samples agree much more nearly in their pressure coefficients than they do in their temperature coefficients. This agrees with previous experience, that in general the temperature coefficient is much more susceptible to impurity than the pressure coefficient. We may expect, therefore, that the pressure coefficient of resistance of pure silicon will be found to be negative, and of the order of -0.000012, pressure being expressed in kg/cm². Compared with most metals, this coefficient is high, being

about the same as that of lead.

Black Phosphorus. Runs were made on two samples of this substance. The first was from the same piece as that which gave the values for the specific resistance and temperature coefficient of resistance already published. The method of formation and some of the other properties have also been described. During the six years since the previous measurements, this specimen has been kept in a glass bottle, closed with a cork stopper and sealed with paraffine. The protection from the action of the air was not perfect, however, because the phosphorus had become covered with a layer of moisture. This moisture is probably due to slow oxidation of the phosphorus in the air. The result of oxidation is the formation of phosphoric acid, which is well known to be very hygroscopic, and therefore rapidly absorbs moisture from the air. An attempt was made to remove the acid from the sample by boiling it with water for a number of hours, and then heating in vacuum for a number of hours in addition.

The specimen previously used was a cylinder about 0.5 inches in

diameter. For the resistance measurements a square prism was cut from the center of this about 0.2 inches on a side. The resistance was measured by the potentiometer method, with the three terminal plug. The terminals were attached to the phosphorus by means of helical coils of very fine wire snapped over the prism in grooves filed on its surface. The distance between potential terminals was about 1.5 cm.

One run was made with this sample, at 0°. The points with increasing pressure ran smoothly, and on decreasing pressure the points with increasing pressure were repeated, except the final zero, where there developed a parasitic e.m.f. so large that further readings were impossible. The general character of the pressure effect was an enormous decrease of resistance under pressure. The results before the parasitic e.m.f. appeared were very nearly the same as those found later with the second sample. The parasitic e.m.f. was ascribed to the imperfect removal of the phosphoric acid, and the specimen was again treated for a number of hours with boiling water, but without success. It was evident that the acid permeated the material too deeply to be removed by surface treatment in this way. It was accordingly necessary to prepare a fresh specimen of phosphorus.

In preparing this fresh sample, advantage was taken of an observation made by Dr. A. Smits 21 in preparing the phosphorus for measurements of the vapor pressure. He found that the kerosene by which pressure had been transmitted to the phosphorus during formation was exceedingly difficult to remove. A chemical analysis by Professor Baxter had also shown some carbon as an impurity of the phosphorus; it is possible that some of this might also have been introduced by the kerosene. It was therefore indicated that the black phosphorus should be formed if possible without contact with kerosene. This was simply done by surrounding the vellow phosphorus with water in the lower cylinder, transmitting pressure to the water with kerosene as usual, but so choosing the dimensions that the kerosene should never come in contact with the phosphorus. This was entirely successful; the transition went essentially as before, when kerosene was used. In particular, occasion was taken to again measure the time rate of transition, and the same results found which have already been published,22 and which make the explanation of the transition from yellow to black phosphorus so puzzling. the phosphorus formed under water was purer than the phosphorus previously formed under kerosene was suggested by the absence of the peculiar odor, which had permeated the earlier product, characteristic of kerosene which has been exposed to high temperatures and pressures. It would be of interest if the vapor pressure measurements of Professor Smits could be repeated on this specimen.

The specimen so formed was dried in vacuum for a number of hours, at 125°, and sealed into an exhausted glass tube until ready for use. It was cut to the same dimensions, and mounted in the same way as the other specimen. Three runs were made with this, at 0°, 51°, and 95°. In addition to the temperature seasoning incidentally done when it was heated in vacuum, it was given a pressure seasoning by an application of 12000 kg. at 0°. The runs all went smoothly; parasitic

TABLE XVII.
BLACK PHOSPHORUS.

Pressure		Resistance	
kg/cm ²	0°	50°	100°
0	1.000	0.662	0.421
1000	.796	.521	.323
2000	.643	.406	.250
3000	.492	.313	.1950
4000	.372	.239	.1517
5000	.277	.1816	.1183
6000	.2042	.1371	.0910
7000	.1493	.1028	.0701
8000	.1079	.0766	.0542
9000	.0783	.0572	.0425
10000	.0565	.0427	.0337
11000	.0409	.0318	.0266
12000	.0297	.0238	.0209

e.m.f.'s were no larger than would be expected from the high thermal e.m.f. of this material, the behavior was perfectly reversible with ascending and descending pressure, and the alteration of zero after a run was no larger than the irregularities of any other of the observed points.

The outstanding feature of the results is the exceedingly large decrease of resistance brought about by pressure, much larger than for any other substance which I have measured. At 0° and 12000 kg, the resistance is only 3% of its value at atmospheric pressure. The ordinary method of plotting is not adapted to such a wide range

of relative values, and accordingly in smoothing the results and making the interpolations and extrapolations involved in making a table of resistance at uniform intervals of pressure and temperature, the logarithm of the resistance was plotted against pressure instead of resistance itself.

Except for two bad points, the maximum departure of any point from a smooth curve at any temperature was 2% of the resistance at that point, and the agreement was usually much closer.

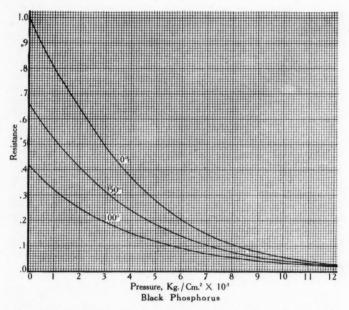


Figure 11. Relative resistances of black phosphorus at several constant temperatures as a function of pressure.

The smoothed results are shown in Table XVII, which gives resistance at 0°, 50°, and 100° at even 1000 kg. intervals, and in Figure 11. The use of significant figures in the table should be mentioned, the number of decimal places not being constant throughout the table. The accuracy of the results justifies only the places shown. The

resistance itself was measured at every point with enough accuracy so that it would have been permissible to keep throughout the table a constant number of decimal places, but the pressure itself at the lower pressures is not known with a high enough accuracy to justify keeping more significant figures than shown.

When the logarithm of resistance is plotted against pressure a nearly linear relation is found at all three temperatures. This means

that $\frac{1}{R} \frac{dR}{dp}$ is approximately constant at all pressures at constant

temperature, where R is the instantaneous value of the resistance at the pressure in question. The instantaneous pressure coefficient is a function of temperature, however. The average value of the instantaneous coefficient between 0 and 12000 kg. is -0.000293 at 0°, -0.000277 at 50°, and -0.000250 at 100°. The deviation of the logarithm from exact linearity changes sign with rising temperature. At 0° and 50° the instantaneous coefficient becomes greater with increasing pressure, which is not what one might expect, whereas at 100° it becomes less. At the two lower temperatures the deviations from linearity run smoothly with the pressure, but at 100° the variations, although much less numerically, show one or two points of inflection with rising pressure. At 0° the initial value of the instantaneous coefficient is -0.000200 and at 12000 kg. it has risen to -0.000320; the corresponding values for 50° are -0.000231 and 0.000290, and for $100^\circ -0.000262$ and -0.000249.

The specific resistance was also determined. At 0° this was found to be exactly 1.000 ohms per cm. cube. This is higher than the value previously published for the other specimen, which was 0.711. The effect of temperature on the new specimen is also greater than on the previous one. The values for this specimen are shown in the table. The resistance decreases with increasing temperature, and the effect is not linear, as of course it cannot be, for otherwise the resistance would become zero at some finite temperature. The coefficient found for the other specimen was also negative, but smaller numerically and within the temperature range, the relation was linear. Previously the relative resistance was found to drop from 1.000 to 0.711 between 0° and 50°, whereas here the drop is found to be from 1.000 to 0.622 for the same temperature interval. In view of the greater precautions in the preparation of this sample, there can be no doubt but that the present values are to be preferred.

It was considered of sufficient interest to measure the thermal e.m.f. of this specimen of black phosphorus. The details of the

method need not be described; they were sufficiently obvious. Asymmetry in the specimen was eliminated by making two sets of readings with the hot and cold ends reversed. The difference of readings in the two positions was only 3%. The temperature interval was from 0° to 21° . The effect is very large. The thermal e.m.f. against copper in this interval was at the rate of 0.000413 volts per degree Centigrade, positive current flowing from copper to phosphorus at the hot junction.

IODINE. The measurements on iodine were part of the systematic attempt to measure the effect of pressure on the resistance of all the elements which could be handled with sufficient ease. The striking effects found for black phosphorus, and the nearness of phosphorus and iodine in the periodic table gave rise to the hope that a similar

effect might be found with iodine.

The measurements proved of unexpected difficulty, because of the readiness with which iodine dissolves in most of the liquids by which pressure can be transmitted. It was found, for instance, that iodine dissolves in kerosene, or petroleum ether, or glycerine. It was a surprise to find that the solutions are fairly good conductors. Considerable effort was spent in devising a suitable method of transmitting pressure to the iodine and getting electrical connections into it. but without much success. In the arrangement finally adopted, the iodine was melted into an open glass cup, provided with two platinum electrodes connected with wires sealed through the base. The cup was placed in a second larger cup, and the wires led up between the inner and the outer cup, and bent over the edge of the outer cup. The upper part of the inner cup was filled with water to a sufficient depth to completely cover the iodine. The outer cup was filled with Nujol, which covered the iodine and water in the inner cup. Connections were made as usual to an insulating plug, this time one of the old single-terminal plugs. The object of the double arrangement of cups was to keep the iodine from contact with the oil, and to keep the water from contact with the insulating plug and any part of the leads, which would otherwise have been short circuited. The arrangement was not satisfactory, for the glass cracked around the platinum leads under pressure, allowing a slight amount of iodine to go into solution in the oil, and furthermore, because of unequal compressibility of the glass and iodine, some water crept between the surface of the glass and the iodine, thus making a short circuit possible. The iodine further dissolved to some extent in the water under pressure, and from the water it again diffused into the surrounding oil, so that there

was a second possibility of short circuit. The initial resistance of the arrangement was of the order of one megohm. Pressure was not pushed higher than 8000 kg., in order not to freeze the water. At this pressure the resistance had dropped to 35000 ohms. There were large polarization effects, and on releasing pressure the resistance did not recover its initial high value.

These experiments can only justify the conclusion, therefore, that under high pressure iodine does not at any rate become metallic in its conductivity, but the specific resistance remains high. It is quite possible that the relative resistance may suffer large changes, but the probability is small that the change of relative resistance is as high as it is for black phosphorus.

The iodine used for this experiment was Kahlbaum's, previously dried in vacuum. The platinum electrodes were approximately 1 cm² each in area, and 3 mm. distance from each other. These dimensions, together with the value of the minimum resistance recorded above, allow a minimum value to be set for the specific resistance at 8000 kg. of about 100,000 ohms per cm. cube. The correct value is doubtless many fold greater. The specific resistance of iodine under ordinary conditions seems too much affected by impurities to allow of its accurate determination, and I have not been able to find a value anywhere recorded.

"CHROMEL A." This is an alloy for high temperature resistance units essentially similar to the alloys known more familiarly under the name of "Nichrome." "Chromel A" is made by the Hoskins Co. of Detroit, and has the composition 80% nickel and 20% chromium. It was furnished by the manufacturer in the form of a wire 0.005 inches diameter, and was double silk covered by the New England Electrical Works. I wound it for these measurements into a coreless toroid of 118 ohms resistance at 0°. It was seasoned for the measurements by keeping it at 135° for four hours, and by a preliminary application of 2000 kg.

The effect of pressure is in the normal direction, that is, the resistance decreases with increasing pressure, but the effect is very small, smaller than any which I have previously found. The maximum displacement of the slider of the Carey Foster bridge was 4 cm., so that the sensitiveness of the measurements was not greater than one part in 400. Within the limits of error the relation between pressure and resistance is linear to a maximum pressure of 12000 kg. At 0° the two points at the highest pressures were irregular, probably because of viscosity in the transmitting medium, and at 90° there were hysteresis effects amounting to 4% of the total pressure effect.

At 0° the pressure coefficient was -0.0_6134 , and at $90^{\circ} -0.0_6137$. The temperature coefficient between 0° and 90° was 0.000163.

"CHROMEL B." This alloy is much similar to "Chromel A." It is made by the same concern, and has a composition of 85% nickel and 15% chromium. Like the previous material it was furnished in the form of wire 0.005 inches in diameter, and was double covered with silk insulation by the New England Electrical Works. It was also wound into a coreless toroid of approximately 100 ohms resistance at 0°. It was seasoned for temperature at the same time as the "Chromel A" by four hours at 135°, but was in addition seasoned for pressure by a single application of 12000 kg. at room temperature, and a single application of 2000 kg. after mounting ready for the measurements.

The general character of the results is the same as for "Chromel A." The coefficient is not quite so small, and the results were considerably more regular. This was in part due to the choice of a less viscous transmitting medium. The relation between pressure and resistance is linear within the limits of error. Two series of measurements were made, at 0° and 95°, to a maximum pressure of 12000 kg. At 0° the maximum departure of any single reading from the linear relation was 1.5% of the maximum effect, and at 95° it was 1.9%, except for the

zero, which showed a displacement of 3.5%.

At 0° the average pressure coefficient was -0.0_6158 , and at 95° -0.0_6169 . The average temperature coefficient of resistance at

atmospheric pressure between 0° and 95° was 0.000212.

"Chromel C." This alloy is also intended for high resistance heating units. It is made also by the Hoskins Co., but unlike Chromel A and B contains some iron in addition to nickel and chromium. The exact composition is Fe 25%, Ni 64%, and Cr 11%. The wire was 0.005 inches in diameter, double silk covered, and wound into a coreless toroid of such dimensions as to have at 0° a resistance of 178 ohms. It was seasoned by one preliminary application of 12000 kg., and after connecting to the pressure apparatus by three applications of 2000 kg. Measurements were made on the Carey Foster bridge, as usual with materials of high resistance.

Three runs were made, at 0°, 52.24°, and 95.88°. The variation of resistance is not throughout linear with pressure and temperature, but shows departures in abnormal directions. The departures from linearity do not run uniformly, so that it was not possible from the three series of readings to construct a table of resistance which could be used by interpolation to obtain the resistance to the limit of accuracy at any temperature and pressure within the range. This alloy would merit further study for its own sake, but an elaborate investi-

gation did not fall within the present program, and the results are given as found.

At 0° the relation between pressure and resistance is linear within the limits of error. The maximum departure of any point from the linear relation was 0.3% of the total pressure effect, and the departures from linearity were distributed at random. The average pressure coefficient of resistance between 0 and 12000 kg, was -0.064272.

At 52.24° the relation between pressure and resistance was again linear within the limits of error, but there was sensible hysteresis. The maximum width of the hysteresis loop was 1% of the total effect. The ascending and descending points all lay smoothly on their respective branches of the hysteresis loop without departures of more than 0.06% of the effect. The average pressure coefficient between 0 and 12000 kg. was - 0.04194, less than the value at 0° .

At 95.88° the relation between pressure and resistance was sensibly not linear, but could be represented within the limits of error by a second degree curve. The maximum departure of any observed point from the second degree curve was 0.35% of the maximum effect. The departure from linearity is in the abnormal direction, that is, the average coefficient between 0 and 6000 is less numerically than the average coefficient between 0 and 12000 kg. The average coefficient 0 to 12000 was -0.0_64488 , and that between 0 and 6000 was -0.0_64372 . It is to be noticed that somewhere between 0° and 100° the pressure coefficient of resistance has passed through a minimum.

The temperature coefficient of resistance at atmospheric pressure is normal in being positive, but the direction of curvature is abnormal. The average coefficient between 0° and 52° is 0.001076, and between 0° and 96° 0.001030.

"COMET" ALLOY. This is an alloy of the following composition:

TANES IN COLUMN	io, or the ros
Cr	1.75%
Ni	31 - 32%
C	.2025%
Si	.2025%
Mn	1.8-2.0%
P and S	very low
Fe	balance

It is made by the Electrical Alloy Co. and was furnished by them in the form of wire 0.005 inches in diameter, and doubly covered with silk insulation. It was wound for the measurements into a coreless toroid of 283 ohms resistance at 0°. Readings were made on the Carey Foster bridge in the usual way at 0°, 51.22°, and 95.32°.

The wire was seasoned by a preliminary application of 12000 kg. at room temperature, and after soldering to the insulating plug, by four additional applications of 2000 kg. at room temperature. That the seasoning was adequate is shown by the fact that there was no further perceptible change of zero after the first excursion to 12000 and back.

The readings showed a small but distinct hysteresis, increasing at the higher temperatures. At 0° the width of the loop is 0.45% of the total pressure effect, at 51° 0.5% of the effect, and at 95° 0.67%. At 95° there was a displacement of the zero after the run of an amount equal to the width of the hysteresis loop. At the other temperatures there was no perceptible change of zero.

The results were computed in the usual way, and are shown in Table XVIII, and Figure 12. This alloy is unusual in that the pres-

TABLE XVIII. "COMET" ALLOY.

Temp. Resistance		Pr	essure Coeffic	Pressure of Maximum	Maximum Deviation from	
		At 0 kg.	At 12000	Average 0-12000	Deviation	Linearity
0	1.00000	-0.0₅263	-0.05222	-0.052413	5000	.00046
50	1.04644	224	206	2176	6500	25
100	1.09061	203	194	2008	6500	7

sure coefficient of resistance becomes less at the higher temperatures, although the resistance itself becomes greater. The behavior is normal in that the pressure coefficient becomes less at the higher pressures at constant temperature. The relation between pressure and resistance becomes more nearly linear at the higher temperatures, which would be unusual for a pure metal.

"Therlo." This is an alloy much like manganin in its properties, made by the Driver Harris Co. The composition is Cu 85%, Mn 13%, Al 2%. It has been used in the high pressure work at the Geophysical Laboratory as a substitute for manganin in high pressure gauges. The sample on which I made measurements was 0.005 inches in diameter, double silk covered, and wound into a coreless toroid of a resistance at 0° of 127 ohms. This was very nearly the resistance of

the manganin pressure gauge, so that a very accurate comparison of the pressure coefficients of manganin and Therlo could be made by plotting on a large scale the difference of the readings with the two alloys. The Therlo was seasoned by one application of 12000 kg. at room temperature, and after soldering to the insulating plug, by four additional applications of 2000 kg.

Three runs were made, at 0°, 51.05°, and 94.80°. The variations with temperature were so slight that the readings could be reduced to regular temperature intervals by an interpolation or extrapolation so short that there was no possibility of error. The resistance of this sample of Therlo did not vary quite linearly with pressure, that is,

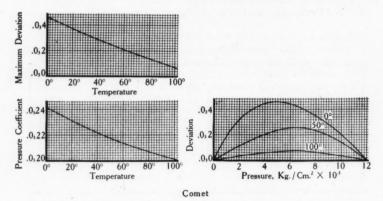


FIGURE 12. Results for the measured resistance of Comet alloy. The deviations from linearity are given as fractions of the resistance at 0 kg, and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

it did not vary linearly with the manganin. (The manganin was originally calibrated against an absolute gauge and found linear within 0.1%). The deviations from linearity of the Therlo are greatest at the lower pressures and are not symmetrical.

At 0° the maximum departure of any single observed point from a smooth curve was 0.09% of the total pressure effect, at 51° 0.14%, and at 95° 0.05%.

The results have been computed in the regular way, and are exhibited in Table XIX and Figure 13. The method of representation is the same as that used in the preceding paper on resistance under

TABLE XIX.
"THERLO."

Temp. °C.	Resistance	Pressure Coefficient Average At 0 kg. At 12000 0-12000		Maximum Deviation from Linearity	Pressure of Maximum Deviation	
0	1.00000	+0.052361	+0.052273	+0.052283	.000112	4000
50	1.00120	2386	2318	2308	112	4500
100	1.00104	2367	2320	2323	83	5000

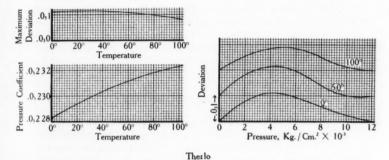


Figure 13. Results for the measured resistance of Therlo alloy. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0° C. The pressure coefficient is the average coefficient between 0 and 1200 kg.

pressure. It will be noticed that the average pressure coefficient shows greater variation with temperature than does that of manganin, and the variations are in fact greater than the variations of resistance itself. The resistance passes through a maximum in the neighborhood of 75°, the increase between 0° and 75° being 0.120%, and between 0° and 100° 0.104%, whereas the average pressure coefficient continues to increase over the entire range between 0° and 100° . The instantaneous coefficient at 0 kg., however, passes through a maximum between 0° and 100° .

"*193 Alloy." This is an alloy containing Fe 68%, Ni 30%, and

 ${\rm Cr}~2\%$, made by the Driver Harris Co. for use in heating units. I was interested in the pressure and temperature coefficients because I had used it as the capillary for containing liquid lithium. The accuracy required in the coefficients was not high, so that measurements of the pressure coefficient at only one temperature and of the temperature coefficient between only two temperatures were sufficient.

The specimen was in the form of a capillary 0.045 inches outside diameter, and 0.032 inches inside diameter, about 6 cm. long. The resistance was too low to be measured by the Carey Foster method, and accordingly the potentiometer was used, as with other metals of low resistance. The temperature of the pressure readings was 94.2°. At this temperature the resistance decreases with increasing pressure, the relation is linear within the limits of error, and the average coefficient between 0 and 12000 kg. is -0.0_51790 . Except for a single bad point, the maximum departure of any reading from the linear relation was 0.7% of the total effect, and the arithmetic mean of all the departures was 0.25%.

The average temperature coefficient of resistance at atmospheric pressure between 0° and 94° was 0.000684.

GENERAL SURVEY OF RESULTS.

We have in the first place to inquire whether these new results for elements somewhat unusual in their properties are the same in character as those previously obtained for the more common elements. In discussing the new data it will be convenient to discuss separately metals in the solid and liquid state, and also metals with positive or negative pressure coefficients of resistance. The previous results were almost entirely for solid metals; measurements for only one liquid metal, mercury, had been made at that time. Furthermore, the pressure coefficient of all solids, except bismuth and antimony, was negative. In the following a solid or liquid is called normal if its pressure coefficient of resistance is negative. The alloys will require separate discussion.

Normal Solids. The normal solids embraced in the present series of measurements are Na, K, Mg, Hg, Ga, Ti, Zr, As, W, La, Nd, Si, and black phosphorus. The special interest of these measurements attaches to those substances with large coefficients. Many of the above list do not belong in this category, and may be dismissed with a few words.

Mg and W were measured in the previous paper. Except for the improvement in the numerical values afforded by the new measurements, these substances require no further discussion. It is to be noticed that the revised values of the pressure coefficient are in such a direction as to make the pressure coefficients of atomic amplitude and resistance even more divergent than was found previously.¹

La and Nd are the first metals of the rare earth group whose pressure coefficients of resistance have been measured. The coefficients of both these substances are not distinguished in any particular way over those of the elements of the previous paper, and do not require

further discussion.

Ti and Zr also belong to a class of elements not previously measured. There was considerable impurity in these materials, and the results have no considerable accuracy. The results are chiefly remarkable for the smallness of the coefficients, which are smaller than for any other pure substances measured. It is even possible that Ti belongs to the abnormal metals, and that its resistance increases with increasing pressure, but the experimental accuracy was not high enough to allow this to be stated with certainty.

Arsenic is a substance which might be expected to show abnormal results because of its position in the periodic table, but it is actually found to be quite normal both in regard to the sign of the coefficient

and its magnitude.

Gallium is another substance for which abnormal results were expected because of its anomalous property of expanding on freezing. The coefficient is however, normal in sign and magnitude. The accuracy of the measurements was not great enough to give the variation of the pressure or temperature coefficients over the range open to measurement.

Solid mercury has been here measured for the first time over a restricted range. It is quite normal with regard to sign and size of

the coefficient.

Silicon and phosphorus are non-metallic in character, and will be discussed later. This leaves of the above list of normal metals only the alkali metals sodium and potassium as needing special comment because of the magnitude of their coefficients. Of the metals previously studied lead was found to have the greatest coefficient, the resistance under 12000 kg. being 14% less than under atmospheric pressure. Contrasted with this is a decrease of over 40% in the resistance of sodium and over 70% in that of potassium under a pressure of 12000 kg. The question is whether substances with such high coefficients

show any change in the usual types of behavior formerly found. The principle facts found before for normal metals were: (1) The pressure coefficient is little affected by temperature, (2) The temperature coefficient is little affected by pressure within the range, and (3) the instantaneous pressure coefficient decreases with increasing pressure (the maximum change in the instantaneous coefficient was that of lead which changed about 30% under 12000 kg.).

Sodium and potassium show no such constancy of behavior, as might be expected from the high values of their compressibilities and pressure coefficients of resistance. Thus for sodium the values of

the instantaneous pressure coefficients $\left[\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_{\tau}\right]$ at 0° at 0, 6000,

and 12000 kg. respectively are -0.0_4663 , 0.0_4435 , and 0.0_4268 , a total decrease by a factor of 2.49. At 80° the corresponding coefficients are -0.0_4786 , 0.0_4466 , and 0.0_4307 , a total decrease by a factor of 2.56. This is a little larger than the factor of decrease at 0°, which is what one would expect. A comparison of corresponding pressure coefficients at 0° and 80° shows the pressure coefficient of sodium is by no means independent of temperature, but the change in the pressure coefficient with temperature is less than the change in resistance itself. The mean temperature coefficient of resistance may also be found from the table of resistance of sodium, and is 0.00475 at $0\,\mathrm{kg}$, and 0.00408 at $12000\,\mathrm{kg}$. The relative change is much large than that found previously for any of the other metals, but still is not large compared with the variations of the pressure coefficient over the same range of pressure.

The same sort of phenomena are seen to characterize potassium, although the coefficients are not known over so wide a range as are those of sodium. At 25° the instantaneous pressure coefficients of resistance at 0, 6000, and 12000 kg. respectively are 0.0₃186, 0.0₄955, and 0.0₄71, a decrease by a factor of 2.62. At 95° the pressure coefficients at 6000 and 12000 kg. are 0.0₃1024 and 0.0₄885, and at 165° the coefficient at 12000 kg. is 0.0₃1027. The pressure coefficient therefore increases markedly with increasing temperature. The mean temperature coefficients between 25° and 60° at 0, 6000, and 12000 kg. respectively are 0.00454, 0.00341, and 0.00184. The decrease is relatively much larger than for sodium, and is nearly as large as the relative decrease in the pressure coefficient over the same range.

The alkali metals sodium and potassium differ, therefore, in the following particulars from the metals previously measured. The

instantaneous pressure coefficient increases with rising temperature and decreases with rising pressure by amounts which, for the range of this work, may amount to a factor between 2 and 3. The temperature coefficient of resistance decreases with increasing pressure by very perceptible amounts, and decreases much more for potassium than sodium.

The decrease in temperature coefficient at the higher pressures is especially significant. One might perhaps expect that at higher pressures the metal would be compressed into an approach toward its behavior at 0° Abs under atmospheric pressure, since the volume may be reduced by pressure to less than its value at 0° Abs. Now as the absolute zero is approached at atmospheric pressure the temperature coefficient of resistance becomes much greater than the reciprocal of the absolute temperature; this is the exact opposite of the behavior found above at high pressures, the temperature coefficient becoming less. The effect of increasing pressure is seen to be merely that of making the part played by temperature of less and less relative importance, which is after all not unnatural from a certain point of view. In the absence of specific information to the contrary it is natural to connect the unusual behavior of sodium and potassium with the large change of volume, and to expect that other metals will show the same sort of behavior under correspondingly increased pressures.

The non-metals Si and P would not be expected to agree in behavior with the metals, but it is interesting, nevertheless, to summarize their behavior. The magnitude of the mean coefficient of Si is about the same as that of lead. The coefficient may increase very largely with increasing temperature, however, and also may apparently increase with increasing pressure. This is quite contrary to expectations, and would seem to indicate an approach to some sort of instability at high pressures; perhaps as the atoms are pushed more closely together there is an approach to metallic conductivity. The variations of the temperature coefficient of silicon are also abnormal. Initially the coefficient is normal in sign, but small numerically; as pressure is increased it reverses in sign. This reversal in sign of the temperature coefficient, unlike the behavior of the pressure coefficient, does not indicate an approach to metallic conductivity. Too great weight should not be attached to these results, because the silicon was impure. However, it is evident that there are some interesting possibilities here, and the measurements should be repeated when it is possible to obtain purer material.

Black phosphorus is remarkable for the great magnitude of the

coefficient, the resistance decreasing to only 3% of its initial value under 120000 kg. In spite of this abnormally large effect, the relative variation with pressure of the pressure coefficient is much less than that of sodium or potassium. The figures have already been given. There is a reversal of behavior with rising temperature. At 0° and 50° the instantaneous pressure coefficient increases with rising pressure, which is not what we would expect, but at 100° the coefficient falls with rising pressure. The temperature coefficient of black phosphorus is abnormal in sign, being negative. The coefficient decreases numerically with rising pressure, at first slowly, but more and more rapidly. From the table of resistance it may be found that the mean temperature coefficient between 0° and 100° are -0.00579, 554, and 299 at 0, 6000, and 12000 kg. respectively. The readings at the higher pressures are not so accurate as the others, so that possibly the rate of fall of the coefficient at high pressures may be too rapid.

Abnormal solids. Previously there were measurements on only two abnormal solids, bismuth and antimony. The results for antimony were not sufficiently accurate to show the variation of pressure coefficient with pressure, but except for this the two metals agreed in that the pressure coefficient increases with increasing pressure and falls with increasing temperature, and the temperature coefficient falls with increasing pressure.

The instantaneous pressure coefficient of lithium increases with rising pressure, having the following values at 0, 6000, and 12000 kg. respectively; 0.0568, 0.0574, and 0.05796. The accuracy of the measurements was not sufficient to establish variations of pressure coefficient with temperature, or of temperature coefficient with pressure within the range. So far as the results are certain, however, the behavior of Li is like that of Bi and Sb.

For calcium the following values may be found from the table of resistance. The instantaneous pressure coefficients at 0° have at 0, 6000, and 12000 kg, the respective values 0.0_4106 , 0.0_4121 , and 0.0_4135 . The corresponding values at 100° are 0.0_592 , 0.0_4107 , and 0.0_4119 . The pressure coefficient therefore increases with increasing pressure, and decreases with rising temperature. The average temperature coefficients of resistance between 0° and 25° are 0.00299, 0.00291, and 0.00281 at 0, 6000, and 12000 kg. respectively, thus decreasing with rising pressure. Within the limits of error the temperature coefficients between 75° and 100° are the same as between 0° and 25°. It would be normal for the temperature coefficients to decrease with rising temperature. In all particulars of comparison, therefore, Ca is like Bi and Sb.

The pressure coefficient of strontium is abnormal. At 0° the instantaneous coefficient varies only little with increasing pressure, but what change there is is a decrease, which is abnormal. The range of values is from 0.04503 to 0.04492. At 50° the pressure coefficient at first increases with rising pressure, which is what we have come to regard as normal for this type of substances, but between 2000 and 3000 kg. passes through a flat maximum, and from there on decreases. The range is from 0.04469 to 0.0451. At 100° the behavior is like that at 50° except that the maximum with pressure is very much more pronounced, and the maximum occurs at 7000 kg. At 100° the initial value of the instantaneous coefficient is 0.04351, the maximum at 7000 is 0.04452, and at 12000 kg. it has dropped to 0.0432. There is, however, nothing abnormal in the temperature coefficient. The average temperature coefficients between 0° and 100° are 0.00383. 0.00311, and 0.00275 at 0, 6000, and 12000 kg. respectively. In respect therefore to the variation of pressure coefficient with temperature and temperature coefficient with pressure strontium is like the other metals with positive coefficient, but the variation of pressure coefficient with pressure is like that of the others over only a part of the range. It is to be remarked that the absolute value of the pressure coefficient of strontium is much higher than that of any other

Summarizing, the behavior of the five abnormal metals, with the exception of the pressure variation of the pressure coefficient of strontium, is alike in that the instantaneous pressure coefficient increases with rising pressure and decreases with rising temperature, and the

temperature coefficient falls with rising pressure.

Carbon, in the form of graphite, is the only other element at present known with a positive pressure coefficient of resistance. Since it is not metallic, comparisons are unprofitable. Furthermore, it was not possible to obtain results that were numerically reproducible. It may be worth mentioning, however, that graphite is like the metals above in that the pressure coefficient decreases with increasing temperature, but that it is different in that the pressure coefficient is very much less at the higher pressures.

Normal Liquids. The only liquid metal previously measured was mercury. It was found for it that the instantaneous pressure coefficient decreases with rising pressure and increases with rising temperature, and that the temperature coefficient decreases with rising pressure and rising temperature. The behavior is in all respects that which appeals to us as normal. It is worth while to give the

numerical values for liquid mercury, since the range of the previous measurements has now been considerably extended. The results are shown in Table XX.

TABLE XX.
LIQUID MERCURY.

Temperature	0 kg.	$\frac{1}{w} \left(\frac{\partial w}{\partial p} \right)_{\tau}$ 6000 kg.	12000 kg.
0°	0.04322	0.04239	
50°	340	253	
100°	. 367	227	
	Average	Temperature Co	efficient
0-25°	0.00096	0.00074	
75–100°	90	65	0.00054

The measurements on liquid sodium did not cover so wide a range as those on liquid mercury, but within the range they show the same characteristics. At 200° the instantaneous pressure coefficients at 0, 6000, and 12000 kg. respectively are 0.04922, 0.04594, and 0.04396. The relative decrease with rising pressure is considerably greater than is the case with mercury, and furthermore, the coefficient itself is considerably greater. The mean temperature coefficient between 180° and 200° is 0.00325 at 0 kg., and 0.00244 at 12000 kg. This decrease is relatively not so large as that of mercury, although the coefficient itself is larger.

Potassium was liquid over a still smaller range than sodium, so that it is not possible to give as complete results. The instantaneous pressure coefficient decreases with rising pressure, the values at 165° being 0.000168 and 0.000136 at 0 and 6000 kg. respectively. The average temperature coefficient between 135° and 165° increases from 0.00322 at 0 kg. to 0.00463 at 5000 kg., which is the reverse of the behavior of liquid sodium and mercury. The variation with temperature of the pressure coefficient is also abnormal. The initial

pressure coefficient of the liquid at 62.5° is 0.0326, and at 165° this

has dropped to 0.0₃17.

Liquid gallium shows a rather large decrease of the instantaneous pressure coefficient with rising pressure. At 30° the values of the coefficient at 0, 6000, and 12000 kg. respectively are 0.0₅640, 0.0₅535, and 0.0₅490. At 100° the corresponding values are 634, 541, and 491. The effect of temperature on the pressure coefficient is therefore relatively slight; at the lower pressures the coefficient decreases with rising temperature, and at the higher pressures it decreases. The mean temperature coefficient of resistance between 30° and 100° changes relatively little, being 0.000815, 829, and 808 at 0, 6000, and 12000 kg. respectively. Compared with sodium and potassium the changes of all the coefficients of gallium are relatively small. It is to be remarked also that the pressure coefficient of gallium is of the same order of magnitude as that of many solid metals; we have come to expect relatively slight variations of the coefficients of those substances with small coefficients.

Liquid bismuth was measured over only part of its region of stability, so that again complete results are not at hand. At 275° the instantaneous pressure coefficient drops from 0.0_4123 at 0 kg. to 0.0_594 at 6000 kg., and at 240° the coefficient is 0.0_592 at 6000 kg., and 0.0_580 at 12000. The temperature coefficient of resistance at 275° drops from 0.00047 at 0 kg. to 0.000453 at 6000 kg. Liquid bismuth is therefore entirely normal in all respects, that is, a falling pressure coefficient with rising pressure and falling temperature, and a falling temperature coefficient with rising pressure. This complete normality is in spite of the fact that solid bismuth is abnormal in having a positive pressure coefficient. The presumption is therefore very strong that the abnormality of the solid is mainly due to the crystalline structure. It is known of course that bismuth crystallizes in the hexagonal system which is not normal, nearly all the elements being cubic.

Summarizing, except for potassium, the behavior of all these liquid metals is of the same type; the pressure coefficient decreases with rising pressure and increases with rising temperature, and the temperature coefficient decreases with rising pressure.

Abnormal Liquids. Only one abnormal liquid, that is, a liquid with a positive pressure coefficient of resistance, is known, liquid lithium. For this the relation between pressure and resistance was linear within the limits of error and the coefficient was independent of temperature between 200° and 240°. A linear relation between

resistance and pressure means a pressure coefficient becoming less at the higher pressures. This is what one might at first expect, but this is the first time that we have found it in a substance with positive coefficient. Since the pressure coefficient is independent of temperature, the temperature coefficient is independent of pressure over the range of the measurements.

Relative Behavior of the Same Metal in the Solid and the Liquid States. This is a matter of considerable importance as suggesting the relative parts played in the mechanism of conduction by the crystalline structure and the properties of the atoms as such. It will in the first place pay to recall the fact already well known that the direction in which the resistance changes when a metal melts is also the direction in which the volume changes. If the metal expands on melting, as is normal, the specific resistance increases on melting, and if the metal expands on freezing, the resistance of the liquid is less than that of the solid. This rule is without exception. Gallium and bismuth are the only two metals known at present in the second class; the data for antimony do not as yet seem well established. In the present work I was able to add lithium to the list of substances which obey this rule. This is of interest, because solid lithium is abnormal.

With regard to the magnitude of the change of resistance on melting there have been a number of theoretical proposals. The inaccuracy of the experimental results has allowed considerable latitude here. Thus theoretical considerations have been based on the assumption that the ratio of the resistance of the solid to that of the liquid is approximately an integer.²³ There is perhaps a tendency for the values to cluster about the figure 2, but it is now certain that within the limits of error the ratio is not integral. Attempts have been made to connect quantitatively the volumes of solid and liquid with the resistance, as would be suggested by the above general rule. Professor Hall 24 has suggested that if the resistance of the solid is extrapolated to such a temperature that the volume expansion is sufficient to bring the volume of the solid up to the volume of the liquid at the melting temperature, the resistance of the solid will be found to be the same as that of the liquid. Of course any such longrange extrapolation must always be open to question, and it is probable that the numerical agreement found is no more significant than the general rule relating to volume already mentioned.

The above measurements under pressure bring out a fact that could not have been known before, namely that the ratio of the resistance of solid to liquid is approximately a constant characteristic of the particular substance, which does not change greatly as pressure and temperature are changed along the melting curve. We now have the figures for the ratio of the resistance of solid to liquid for six metals at different pressures and temperatures. For lithium the accuracy was not high enough to permit more than the statement that the ratio does not change greatly in a pressure range of 8000 kg. For sodium the ratio is 1.45 at atmospheric pressure, and has dropped to 1.36 on the melting curve at 12000 kg. The difference of volume between solid and liquid has dropped to half its initial value in the same pressure range, so that the ratio of resistances is evidently more constant than the difference of volume. For potassium the ratio of resistance of liquid to solid is 1.56 at 0 kg., and has dropped only to 1.55 at 9700 kg. Contrasted with this almost negligible change in the ratio of the resistances is a decrease under 9700 kg, of the difference of volume between solid and liquid to 0.31 of its initial value. For mercury, I determined the ratio of resistance of liquid to solid at the melting point at 0° and 7640 kg. to be 3.345. I did not make measurements at any other temperature but there are values by other observers. Onnes 25 finds 4.22, Bouty and Cailletet 26 4.08, and Weber 27 gives 3.8 as the mean of six determinations, all for the ratio at the freezing point at atmospheric pressure. The error is so large that it is not possible to say more than that the change in the ratio along the melting curve is not large, and is in the direction of a decrease with increasing pressure. The change is probably greater than the change in the difference of volume between solid and liquid, which is abnormally constant for mercury, there being a decrease in the difference of only 1% over the pressure range of 7640 kg. The change in the resistance of the liquid over this range is, however, 19%, which is probably larger than the change in the ratio of the resistance of liquid to solid.

The behavior of the two abnormal metals gallium and bismuth is similar. At 7000 kg. I found the ratio of the resistance of liquid to solid bismuth to be 0.45, and at atmospheric pressure Northrup and Sherwood ¹⁶ found 0.43. The ratio is probably constant within the limits of error. For Gallium I found 0.58 for the ratio at atmospheric pressure, and calculated the value at 12000 kg. to be 0.61. This again is perhaps to be regarded as constant within the limits of error, but it is noteworthy that the little variation there is is in the same direction for both gallium and bismuth, and is toward an increase with rising pressure, whereas what variation there was for normal metals was always in the direction of a decrease with rising pressure.

We now compare the relative magnitudes of the pressure and

temperature coefficients of solid and liquid. With regard to the temperature coefficients at atmospheric pressure it has long been known that the coefficient of the liquid is less than that of the solid. This is verified for all the metals measured here, except potassium.

With regard to the pressure coefficient of resistance it is natural to expect that of the liquid to be greater than that of the solid at the same temperature. This is true for sodium. At 120° the pressure coefficient of the liquid is about 7% greater than that of the solid extrapolated to the same temperature. It is however, perhaps surprising that the relative change of the pressure coefficient of solid sodium brought about by an increase of pressure of 12000 kg, is greater than that of the liquid under the same increase of pressure. The relative decrease of the temperature coefficient under 12000 kg, is greater for liquid sodium, however, than for the solid.

liquid sodium, however, than for the solid.

The behavior of liquid potassium is not as we would expect. At the melting point at atmospheric pressure the pressure coefficient of liquid potassium is greater than that of the solid. Because of the abnormal temperature coefficient of the pressure coefficient of the liquid, however, the coefficient of the solid would become greater than that of the liquid if the solid could be superheated sufficiently. The relative variation with pressure of the pressure coefficient is greater for the solid than the liquid. This again is not what we might expect. The data for potassium do not cover a sufficient range to permit a comparison of the variation with pressure of the temperature coefficients

of solid and liquid.

The pressure coefficient of solid mercury has been found to be constant over the range from 7640 to 12000 kg. The coefficient of the liquid, on the other hand, decreases with rising pressure. It has already been mentioned as surprising that the coefficient of the solid is greater than that of the liquid at 6500 kg. This difference would become still more accentuated if the liquid could be carried in the metastable state into the region of stability of the solid; in this range its pressure coefficient would be found to vary considerably less than that of the solid. The measurements were not accurate enough to permit a comparison of the variations of the temperature coefficients of the solid and liquid. It is known, however, that at atmospheric pressure the temperature coefficient of the solid is normal, while that of the liquid is abnormally low even for a liquid.

The pressure coefficient of solid gallium is of the order of 2.5 less than that of the liquid. The coefficient of the solid is independent of the pressure, whereas that of the liquid decreases markedly with increasing pressure. Measurements were not made on the variation with pressure of the temperature coefficient of the solid.

Comparison cannot properly be made between liquid and solid bismuth, because the solid is abnormal and the liquid is normal. It is interesting, however, that numerically the coefficient of the solid is greater than that of the liquid. This may mean that some of the tendency to abnormality still persists in the liquid, making its coeffi-

cient lower than it would otherwise be.

Lithium is abnormal in both liquid and solid. If the data for the solid are extrapolated from 100° to the melting temperature at 180° the figures given would indicate a pressure coefficient of the solid numerically less than that of the liquid. The difference would be still further accentuated if the unknown correction for the compressibility of the solid is applied so as to make the coefficients of both solid and liquid the coefficients of specific resistance. Although the coefficient of the liquid is greater than that of the solid, its variation with pressure is much less, and in fact is opposite in sign, the coefficient of the liquid becoming smaller at higher pressures, and the coefficient of the solid becoming greater. The temperature coefficient of liquid lithium is independent of pressure to 12000 kg., as is that of the solid also.

Summarizing the relations between the coefficients of the liquid and the solid, except for the temperature coefficient of the liquid being less than that of the solid, there does not seem to be a tendency to any one type of behavior. It is noteworthy, however, that in many cases the resistance of the liquid responds more sluggishly to changes of pressure than does that of the solid, the coefficient of the liquid being actually less than that of the solid, or else the change of coefficient

with pressure being less for the liquid.

Alloys. The above data on alloys are entirely unsystematic and fragmentary, so that it is not possible to draw any conclusions as to the behavior of alloys in general. It is interesting to notice, however, that the pressure coefficient of all the alloys, with the exception of that of "Comet," is less numerically than would be computed by the law of mixtures from the coefficients of its components, and in the case of "Therlo" this tendency to a lower value may go so far as to reverse the sign. In making this statement I have assumed that the pressure coefficient of pure Chromium and Manganese is negative, a conclusion which has not been checked by experiment, but which seems very probable from the behavior of similar metals.

THEORETICAL BEARINGS.

Since the purpose of this paper is primarily the presentation of new data, I cannot more than touch on two matters of theoretical interest suggested by considerations of the previous papers.

It has been known for some time that the temperature coefficient at constant volume of liquid mercury is negative instead of positive, as is the coefficient at constant pressure. In my previous theoretical paper ²² I suggested reasons for this. It is now of interest to find whether the other liquid metals have the same property.

The coefficient of resistance at constant volume is given by the relation

$$\left(\frac{\partial w}{\partial \tau}\right)_v = \left(\frac{\partial w}{\partial \tau}\right)_p - \left(\frac{\partial w}{\partial p}\right)_\tau \frac{\left(\frac{\partial v}{\partial \tau}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_\tau}$$

Hence in addition to the pressure and temperature coefficients of resistance, which have been determined in the present work, values of the thermal expansion and compressibility are also needed. These have not been determined experimentally for any of the metals above, but in some cases an indirect estimate may be made with the help of various data from the melting curve. I have previously given an estimate of the difference of compressibility and thermal expansion between solid and liquid sodium, potassium, and bismuth.²⁸ With these data, the temperature coefficients at constant volume may be computed, as is shown in Table XXI. The fundamental data are

TABLE XXI.

The Temperature Coefficient at Constant Volume of Liquid Metals at their Melting Points.

Substance	$\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T$	$\frac{1}{v} \left(\frac{\partial v}{\partial \tau} \right)_{\mathbf{p}}$	$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_{\tau}$	$\frac{1}{w} \left(\frac{\partial w}{\partial \tau} \right)_p$	$\frac{1}{w} \left(\frac{\partial w}{\partial \tau} \right)_{\boldsymbol{v}}$
Sodium	-0.04186	+0.03344	-0.0488	+0.00325	+0.00170
Potassium	-0.04358	.03340	-0.03204	0.0044	+0.0025
Bismuth	-0.0532 (?)	.0312 (?)	-0.0412	0.000475	+0.0415

exceedingly uncertain, because in addition to the uncertainties in the differences of compressibility and thermal expansion between solid and liquid, the compressibilities and thermal expansions of the solids themselves at the melting points are in doubt, the actual measurements having been made in most cases only at room temperature. I have had to guess what the temperature variation of the compressibility might be. However, the uncertainty cannot be so large as to change the sign of the effect for sodium and potassium, for which there can be no doubt that the temperature coefficient at constant volume, as well as the coefficient at constant pressure, is positive. This is the reverse of the behavior of mercury. The data for bismuth are in much more doubt, however. Assuming the figures shown, the coefficient at constant volume is also positive, but the uncertainty is so great that the sign might well be negative.

The coefficient at constant volume of liquid lithium is of course positive, since the pressure coefficient at constant temperature is abnormal in being positive. The data are not at present known for gallium, so that it is not possible to make any sort of an estimate as to the probable value of its coefficient at constant volume.

The outcome of this investigation, therefore, for the only two metals for which the results can be sure, is to reverse the behavior previously found for liquid mercury. In this connection it is to be remarked that the temperature coefficient at constant pressure of liquid mercury is abnormal in being very low, and the corresponding coefficients of liquid sodium and potassium are abnormal in being very high. It does not yet appear, therefore, what the probable value of the constant volume coefficient would be for the more usual metals, such as lead.

The second point of theoretical interest brought out in the previous discussion was the intimate connection between the changes of resistance and the amplitude of atomic vibration. It appeared that the relative change of resistance, whether brought about by a change of pressure or of temperature, was approximately equal to twice the relative change of amplitude under the same change. The relation was by no means exact, there being failures by as much as a factor of two in some cases, but on the average the agreement was rather good for a large number of metals. The question is whether these new elements also show the same relation?

In making the computation the following formula for the change of amplitude with pressure was used

$$\frac{1}{a} \left(\frac{\partial a}{\partial p} \right)_{\tau} = - \frac{1}{C_v} \left(\frac{\partial v}{\partial \tau} \right)_p,$$

where α is atomic amplitude, and C_{\circ} specific heat at constant volume per unit volume. It is therefore necessary to know the thermal expansion and specific heats of the new elements. Unfortunately the data are not known for a number of the metals of this work. The computation has been made for all those normal substances for which the data are available, and the results are collected in Table XXII.

TABLE XXII.

Comparison of the Changes under Pressure of Resistance and Amplitude of Atomic Vibration.

Substance	$\frac{1}{v}\left(\frac{\partial v}{\partial au}\right)_{m p}$	Cv Kg. cm./cm.3	$\frac{2}{\alpha} \left(\frac{\partial \alpha}{\partial p} \right)_{\tau}$	$\frac{1}{w}\left(\frac{\partial w}{\partial P}\right)_{\tau}$
Solid Na, 20°	0.03217	11.1	-0.0439	-0.0468
Liquid Na, 98°	.03344	10.6	-0.0465	-0.0491
Solid K, 20°	.03248	6.48	-0.0476	-0.03186
Liquid K, 63°	.03341	6.64	$-0.0_{3}102$	-0.0326
Liquid Hg, 0°	.03181	17.1	-0.04211	-0.04358
Arsenic	.0416	26.7	-0.0 ₅ 12	-0.0533
Magnesium	.0478	17.7	-0.0 ₆ 88	-0.0548
Tungsten	.04101	27.6	-0.0674	-0.05143

In this table are included the recomputed values for Mg and W. The best agreement is for liquid bismuth. In nearly all the other cases the computed value is much lower than the observed. This is a reversal of the behavior shown by the previous substances, for which in the majority of cases the computed value was too high.

The table seems to show no essential difference between a solid and a liquid metal as far as the connection with amplitude goes.

There seems to be no reason to modify the previous conclusion, which was that in a large way the changes of amplitude of atomic vibration are an exceedingly important factor in affecting changes of resistance. Superposed on this large effect common to all metals, are specific effects, such as peculiarities of atomic structure or arrange-

ment. In particular the factor of atomic arrangement is responsible for the difference between a solid and a liquid metal, and may be so important in some cases as to control the sign of the effect.

SUMMARY.

In this paper results are given for the effect of pressure and temperature on the resistance of twenty elements and several alloys. Endeavor was made to choose elements from unusual places in the periodic table, and also to investigate more fully the behavior of liquid metals.

The resistance of the same metal in the liquid and the solid state has now been measured for six elements. The temperature coefficient of the liquid is less than that of the solid except for potassium. The change of resistance on melting invariably follows the direction of the change of volume. The ratio of resistance of liquid to solid is approximately constant along the melting curve, although the difference of volume may change greatly. The pressure coefficient of the liquid is in some cases less than that of the solid. Liquid bismuth has a negative pressure coefficient of resistance, and is normal, but liquid lithium has a positive coefficient, and is the only such liquid metal yet found. The new liquids do not show a negative temperature coefficient of resistance at contant volume, as did liquid mercury.

The alkali metals sodium and potassium are remarkable for the large changes of resistance under pressure. The pressure coefficient decreases greatly with increasing pressure, and decreasing temperature. The temperature coefficient may decrease greatly with increasing pressure. The variations of these coefficients for the metals investigated.

gated in the previous paper were always small.

Three more solid elements have been found with positive pressure coefficients of resistance; lithium, calcium, and strontium. Of these the pressure coefficient decreases with increasing temperature, the temperature coefficient decreases with increasing pressure, and, except for strontium, the pressure coefficient increases with increasing pressure.

Of the non-metallic elements, black phosphorus is remarkable for a very large negative coefficient, the resistance under 12000 kg. dropping to only 3% of its initial value; silicon has a negative coefficient which becomes numerically larger with increasing pressure, and carbon has a negative coefficient in the amorphous state, and a positive coefficient in the graphitic state, which decreases greatly with increasing pressure.

The additional evidence from these new materials still gives every reason to think that the amplitude of atomic vibration is the largest single factor in determining the changes of resistance under pressure or temperature.

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